SOME REACTIONS OF ORGANOMETALLIC

π-COMPLEXES

A thesis submitted by

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Finally, my thanks go to Dr. J.M. Brown for his continuous help and guidance which I have found invaluable.

SUMMARY

The work of this thesis is in two parts. The first is concerned with the problem of producing the perfume base, muscone, from inexpensive, readily available precursors.

Previously it had been shown that zero-valent nickel complexes would cyclotrimerise butadiene; an intermediate in the reaction being a twelve carbon bis π-allyl complex. The object of the work was to attempt to use this intermediate to produce a fifteen membered carbocycle which could readily be converted into muscone or some other related compound. The preparation and characterisation of the intermediate is described, together with the experimental approach to the problem. Although the work was not successful in producing significant amounts of a fifteen-membered carbocycle, some insight was gained into the reactivity of the π-allyl groups.

The second part of the thesis is concerned with bonding modes and hydrogen shifts in cycloheptatriene complexes with transition metals.

The preparation and characterisation of the previously unknown h^1,h^2 complex, cycloheptatriene rhodium acetylacetonate, is described, together with some of its reactions. Hydrogen shifts in this compound are considered and compared with those in cycloheptatriene iron tricarbonyl and in both cases appears to be non-specific. The complexes are also considered as offering possible routes for the synthesis of $[^2H_7]$ and $[^2H_8]$ cycloheptatriene.

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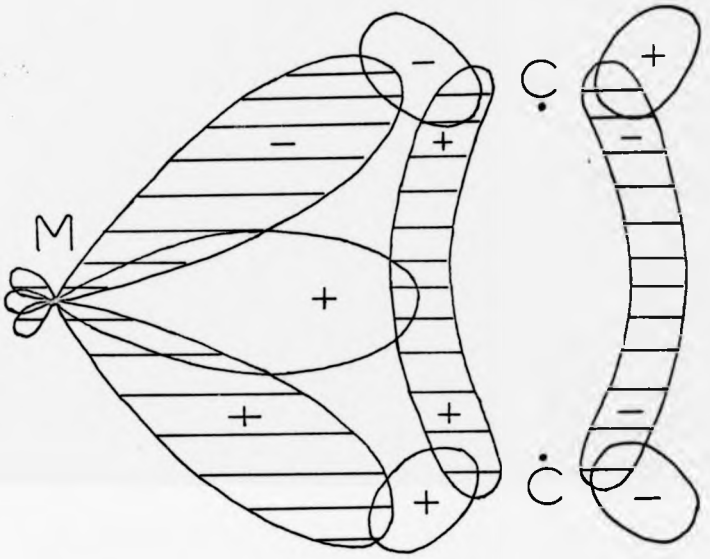

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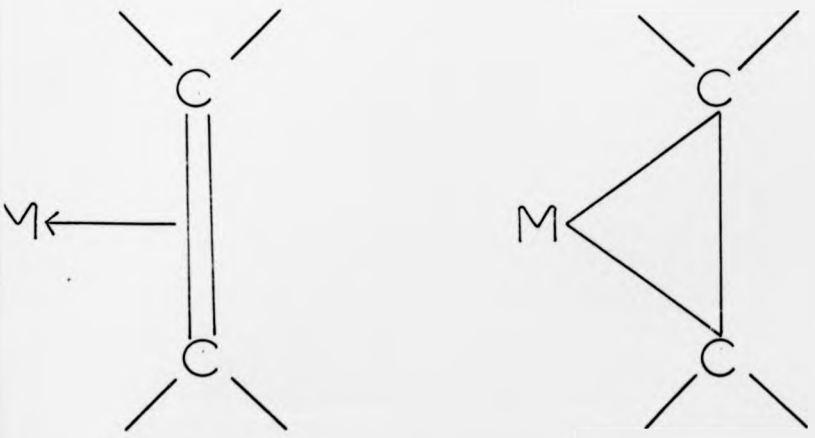

[a] [b]

[2]

INTRODUCTION

The first organometallic olefin complex, $K(C_2H_4PtCl_3)H_2O$ was prepared in 1827 by Zeise [1] and is known as Zeise's salt. Analagous substances were subsequently prepared using propylene and cyclohexene.[2]

Large numbers of olefin complexes are now known to be formed with transition metals, particularly those with filled or almost filled d shells.

A great deal of work has been done on the chemistry of these olefin complexes and in a large number of cases it has been shown that the chemistry of the olefin has been significantly altered by combination with a metal atom. Much of this effect is brought about by the nature of the metal olefin bond.

This bond, as proposed by Dewar [3] and Chatt & Duncanson [4] was considered as being essentially of 2 parts: (a) a σ bond, formed by transfer of charge from a filled $2p\pi z$ molecular orbital of the olefin, to a vacant orbital of suitable symmetry on the metal and (b) a π bond, formed by back donation of charge from filled, non-bonding, dxy orbitals on the metal into empty $2p\pi z^*$ antibonding orbitals of the olefin, (1). However, this theory of the bonding gives a simplified picture of the actual situation. The two extreme modes of bonding in the Dewer-Chatt & Duncanson model are shown in (2). In (2a) the bond from the olefin is pure p in character and the olefinic carbon atoms are sp^2 hybridised, while in (2b) the bonding is sp^3. ^{13}C N.M.R. studies on the coupling constants $J(^{195}Pt, ^{13}C)$[5] and $J(^{103}Rh, ^{13}C)$[6] for a series of olefins, together with photoelectron spectroscopy studies on binding energies of electrons in platinum-olefin complexes[7] indicate that there is no sharp boundary between (2a) and (2b) but suggest that on co-ordination to the metal the olefinic carbon atoms undergo rehybridisation to give molecular orbitals which lie somewhere between sp^2 and sp^3.

Bond lengths in the butadiene molecule (Å)

	Free in ground state	Free in 1st excited state	$C_4H_6Fe(CO)_3$	$C_4H_6Fe(Cp)$
C_1-C_2	1·36	1·45	1·41	1·49
C_2-C_3	1·45	1·39	1·40	1·37
C_3-C_4	1·36	1·45	1·41	1·49

[TABLE 1]

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Mason[8] has shown that there is a close correlation between the geometry of olefins complexed to metals and the geometry of the free olefins in their first excited state. (The bond length values for butadiene are shown in Table 1). This suggests that the wave function for the metal olefin bond is formed by combination of the metal orbitals with those of the olefin in the first excited state.

The amount of s character in the metal-olefin bond will reflect the degree of back bonding from the metal to the olefin. The degree of back bonding to the olefin will depend on the relative energy levels of the donor and acceptor orbitals, since their orbital symmetries must be closely matched in order to achieve overlap for bonding. Therefore, while metals in low or zerovalent oxidation states will transfer charge back to the olefin, those in high oxidation states are unable to do so because their d orbitals have contracted and are no longer of a suitable energy for overlap with the olefin. In addition, like the transition metals containing few d electrons, the electron density at the metal may be insufficient for back donation to occur. The electron density at both the metal and the olefin will be affected by substituent groups, and this will, in turn, affect the mode of bonding. The presence of electron donating substituents on the olefin will increase the σ bonding capacity, while electron withdrawing substituents will increase the π bonding by allowing the metal to feed back more of the charge to the olefin. Electron withdrawing substituents on the metal will, however, decrease the amount of π bonding, by removing electron density from the metal, while electron donating groups attached to the metal will increase its electron density and so enhance the π bonding.

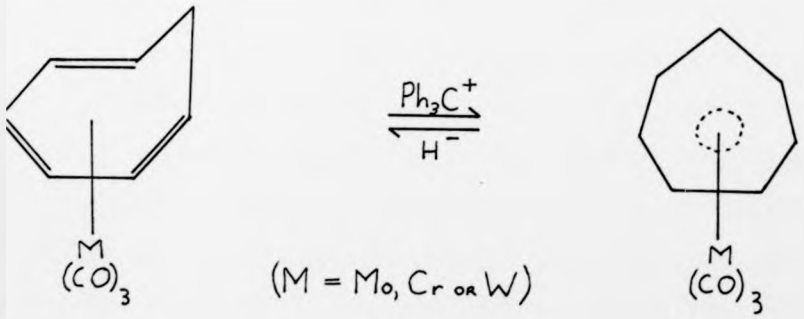
The degree of π back bonding from metal to olefin is reflected in both the infra-red stretching frequency of the olefin bond, ($\nu_{C=C}$), and in the proton nuclear magnetic resonance τ value of the olefinic protons. In the

former, increase in π character of the metal olefin bond results in a decrease in νc=c due to an increase in antibonding character, while in the latter case increase in π character causes an increase in the τ value due to a higher degree of shielding of the olefinic protons. ^{13}C N.M.R. studies[5] indicate similar shielding effects for the olefinic carbon atoms. Thus both I.R. and N.M.R. techniques can be used to determine the relative σ and π contributions for a series of metal olefin complexes. Thus in bis(ethylene)rhodium acetylacetonate, $[(C_2H_4)_2Rh$ acac$]$, replacement of the ethylene groups by 1,2 difluoroethylene results in a decrease in νc=c and an upfield shift in the N.M.R. spectrum of the olefinic protons. Replacement with tetrafluoroethylene causes an even larger decrease in νc=c. This is due to the negative inductive (i.e. electron withdrawing) effect of the halogen reducing the energy level of the π^* antibonding orbitals of the olefin and so allowing more back donation of charge from the metal resulting in the metal-olefin bond having greater π character. The σ character of the bond is reduced since the electronegative substituents withdraw some of the charge from between the carbon atoms of the olefinic bond. Alkyl substituents on the olefinic carbon atoms induce a deshielding effect on the olefinic protons[9] by raising the energy level of the olefinic π^* antibonding orbital and hence decreasing the amount of back bonding from metal to olefin. Since alkyl substituents have a positive inductive effect, (i.e. they are electron donating) they will increase the charge between the olefinic carbon atoms and so enhance the σ componant of the metal-olefin bond. Replacement, by tetrafluoroethylene, of one of the ethylene groups in $(C_2H_4)_2Rh$ acac, to form $(C_2F_4)(C_2H_4)Rh$ acac[10], causes an increase in νc=c of the remaining ethylene and a shift to lower field in the N.M.R. spectrum of its protons indicating a decrease in back bonding from the metal to the ethylene. In this case, the tetrafluoroethylene being a strong π acid, is acting as an electron withdrawing ligand

on the metal so reducing its charge density and decreasing the π character of the metal-ethylene bond. Replacement, by the cyclopentadienyl group, of acetylacetonate in bis(ethylene)rhodium acetylacetonate, causes an increase in the π component of the metal-olefin bond since the cyclopentadienyl group, being electron releasing, increases the charge density on the metal, allowing it to become a more effective electron donor.

Most metals which form complexes with olefins have almost filled d shells and when complexed are usually in a low oxidation state. Thus they have a relatively high electron density, with the result that the π component of the metal-olefin bond tends to predominate. However, in complexes of olefins with silver and most other metals of group IB, the σ component predominates. Thus when a mono-olefin co-ordinates to most metals the olefinic protons are shielded, indicating a nett transfer of charge from the metal to the olefin caused by a predominance of π character. However, co-ordination to silver results in a deshielding of the olefinic protons[11] indicating a nett transfer of charge from the olefin to the metal, resulting from predominant σ bonding. Also, a comparison of the stabilities of rhodium and silver olefin complexes shows that for rhodium, electronegative substituents on the olefin stabilise the rhodium complexes, while alkyl substituents destabilise[12]. Thus tetrafluoroethylene forms a much stronger bond with rhodium than does propylene. However, with silver complexes, alkyl substituents stabilise while electron-withdrawing substituents destabilise. Thus for complexes of the type $(olefin)_2 AgBF_4$, the relative stabilities are in the order propylene $>$ ethylene $>$ vinyl chloride[13]. This indicates that, in the silver-olefin bond, there is a far greater dependance on the electron-donor properties of the olefin and that therefore the σ component predominates. ^{13}C N.M.R. studies also suggest that back-donation, from metal to olefin, is unimportant in bis(propene)silver tetrafluoro-borate, but that it is important in both bis(propene)rhodium acetylacetonate and propene iron cyclopentadienyl-dicarbonyl[14].

[3]



(M = Mo, Cr or W)

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Reactions of metal-olefin complexes

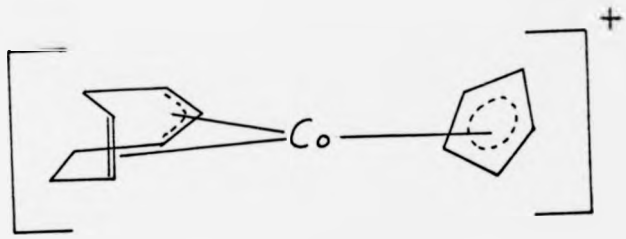
Clearly the bonding in olefin metal complexes will affect the reactivity of the olefin. Thus an increase in the σ bonding component will, by transferring more charge from the olefin to the metal, make the olefin more susceptible to nucleophilic attack, (and the metal more susceptible to electrophilic attack), while an increase in π back-donation will transfer more charge to the olefin and thus enhance electrophilic attack.

Reactions with electrophiles

Electrophilic reactions of metal-olefin complexes usually involve protonation by reaction with acid (H^+), or hydride abstraction by reaction with 'trityl', the triphenylmethyl cation, Ph_3C^+.

Protonation reactions normally occur at the site of greatest electron density. If the metal is electron-rich relative to the olefin then protonation will occur on the metal and if the olefin has the higher electron density, then it will be the site of attack. Thus olefin-metal complexes in which there is a high degree of back-donation from metal to olefin (i.e. a strong π component) will tend to protonate on the olefin. Hence olefins co-ordinated to rhodium or iron are susceptible to electrophilic attack by acids. e.g. $[RhCl(CO)(C_2H_4)]_2$ readily adds HCl to give $[RhCl(CO)(C_2H_5Cl)]_2$ [15] and the butadiene complex $(C_4H_6)Fe(CO)_3$ undergoes protonation with HCl to give the π-crotyl complex $C_3H_4(CH_3)Fe(CO)_3Cl$ [16]. However, while the iron complex $(C_8H_8)Fe(CO)_3$ is protonated in concentrated acids to give the cation $[(C_8H_9)Fe(CO)_3]^+$ [17], [3], the cyclooctatetraene rhodium complex, $C_8H_8RhC_5H_5$, does not undergo protonation under these conditions. This is mainly due to a difference in the mode of bonding of the olefin to the two metals. In the iron complex, the olefin bonds as a 1,3 diene in a tetrahapto (h^4) conjugated fashion, (although the situation is complicated by 'ring whizzing'), whereas in the rhodium complex it bonds as a 1,5 diene in an h^2,h^2 non-conjugated fashion which is unreactive towards H^+.

In general, protonation of olefin which in most cases will not form a



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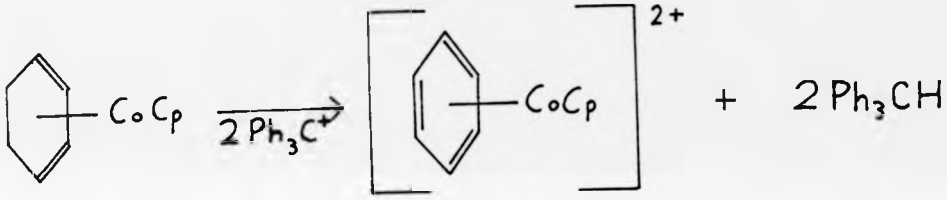

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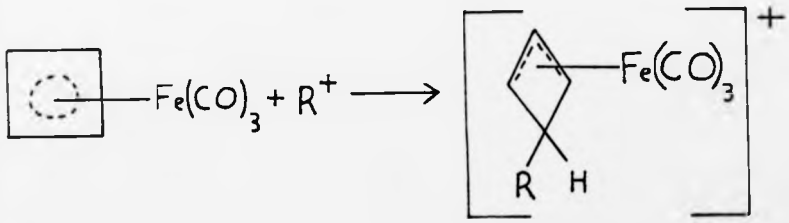
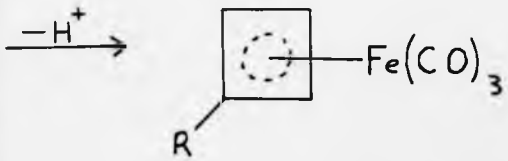




[7]

stable cation in the free ligand, will occur when it is complexed to a metal in a low oxidation state due to stabilisation of the carbonium ion by transfer of charge from the metal.

Hydride abstraction reactions occur with a wide range of metal-olefin complexes, as electrophilic attack by Ph_3C^+ generated from triphenylmethyl tetrafluoroborate. This species is particularly useful in hydride abstraction because of the stability of the carbonium ion. Thus cycloheptatriene complexes of chromium, molybdenum and tungsten react with Ph_3C^+ to produce cycloheptatrienyl derivatives.[4]. However, the Ph_3C^+ will only react by abstracting the 7-exo-hydrogen of the methylene group in cycloheptatriene[18], i.e. the reaction is stereospecific. Thus, while 7-endomethylcycloheptatriene chromium tricarbonyl undergoes hydride abstraction with Ph_3CBF_4, 7-exomethyl-cycloheptatriene chromium tricarbonyl does not.[18,19]

1,5-cyclooctadiene cobalt cyclopentadienyl, (1,5-COD)Co(π-C_6H_5) reacts with triphenylmethyl fluoroborate to give the cycloocta-2,5-dienyl cation [5][20]. With 1,3-cyclohexadiene cobalt cyclopentadienyl, the arene complex $[(C_6H_6)Co(C_5H_5)]^{2+}$, [6], is formed.[21]

The cations formed in the above hydride abstraction reactions will readily react with a variety of nucleophiles to give monosubstituted deriviatives of the original metal olefin complexes. Thus the cycloheptatrienyl cation, $[C_7H_7Cr(CO)_3]^+$, will react with methoxide ion, (MeO^-), to form 7-exo-methoxycycloheptatriene chromium tricarbonyl[19], while the cyclooctadienyl cation [5] readily reacts with cyanide ion to produce the substituted diene[20]. Therefore the hydride abstraction can be considered as the first step in a two step electrophilic substitution reaction.

Metal-olefin complexes in which the olefin is essentially aromatic also undergo electrophilic substitution reactions. Cyclobutadiene iron tricarbonyl and its derivatives show aromatic character by undergoing reactions analagous to Friedel-Crafts acylation [7][22]. Although benzene, when complexed to a metal, will undergo electrophilic substitution, it is much more reluctant to do so than is the free arene. This is partly due to electron

(a) $PdCl_4^{2-} + C_2H_4 \longrightarrow PdCl_3(C_2H_4)^- + Cl^-$

(b) $PdCl_3(C_2H_4)^- + H_2O \longrightarrow trans\ PdCl_2(C_2H_4)H_2O + Cl^-$

(c) $PdCl_2(H_2O)(C_2H_4) + H_2O \longrightarrow PdCl_2(OH)(C_2H_4)^- + H_3O^+$

(d) $PdCl_2(OH)(C_2H_4)^- \longrightarrow HOCH_2CH_2PdCl + Cl^-$

(e) $HOCH_2CH_2PdCl \longrightarrow CH_3CHO + Pd + HCl$

[SCHEME 1]

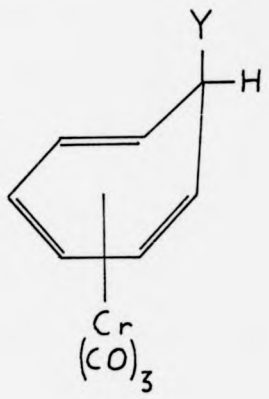
transfer from the ring to the metal resulting in deactivation of the ring.[23]

Reactions with Nucleophiles

In many cases an olefin may be made more susceptible to nucleophilic attack by combination with a transition metal. Nucleophilic attack occurs at sites of relatively low electron density and therefore, on formation of the complex, there should be a net movement of charge from the olefin to the metal. In other words, the σ component of the metal-olefin bond will predominate. Thus combination of the olefin with a cationic metal species would be expected to enhance nucleophilic attack on the olefin, as would the presence of electron withdrawing groups on the metal.

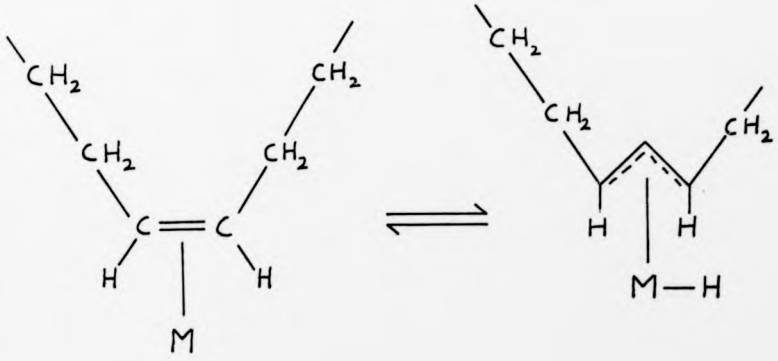
On reaction with lithium aluminium hydride, the hexamethylbenzene tricarbonyl rhenium cation, $[C_6(CH_3)_6]Re(CO)_3$, forms the hexadienyl complex, $[C_6(CH_3)_6H]Re(CO)_3$, by hydride addition[24]. Similarly the ethylene cyclopentadienyl iron dicarbonyl cation, $[(C_2H_4)Fe(CO)_2(C_5H_5)]^+$, also undergoes hydride addition with sodium borohydride to form the ethyl iron complex, $(C_2H_5)Fe(CO)_2(C_5H_5)$[25]. The fact that co-ordinated ethylene is susceptible to nucleophilic attack is made use of commercially in its catlylic oxidation to acetaldehyde, using palladium dichloride. An ethylene-palladium complex is formed which is then readily attacked by hydroxide ion, [SCHEME 1][26].

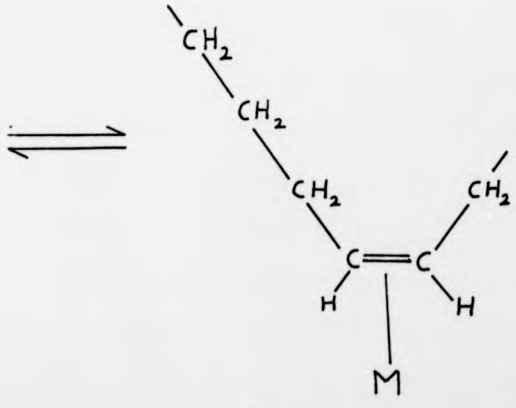
As with electrophilic attack on metal olefin complexes, the site of nucleophilic attack can be determined by other ligands attached to the metal. Thus the cyclopentadienyl iron tricarbonyl cation, $[Fe(CO)_3(C_5H_5)]^+$, undergoes nucleophilic reaction with hydride iron to form $HFe(CO)_2(C_5H_5)$, whereas the cation, $[Fe(CO)_2PPh_3(C_5H_5)]^+$, undergoes hydride addition to give $Fe(CO)_2PPh_3(C_5H_6)$. In the first case nucleophilic attack occurs at the metal, whereas in the second, it occurs at the cyclopentadienyl ring, forming the diene complex. The difference is, to a large extent, due to the triphenylphosphine group being electron releasing, which decreases the



Y=(I, Br, MeO, EtO)

[8]



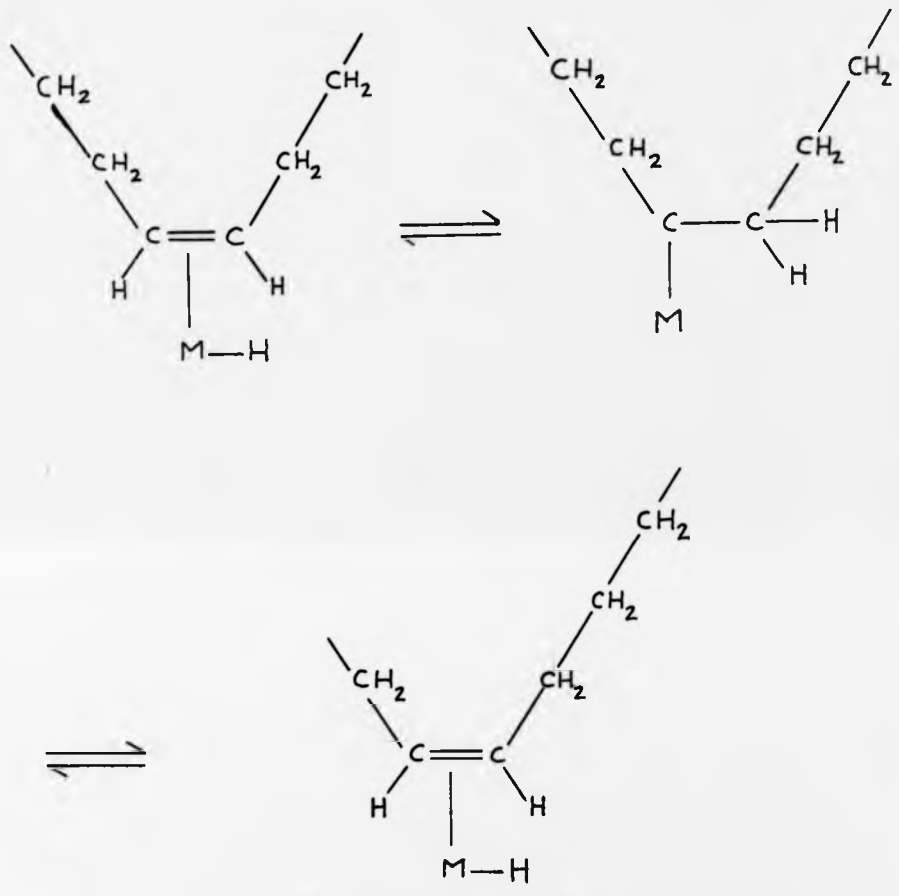


[SCHEME 2]

positive charge on the metal and leaves the cyclopentadienyl group as the site of lowest electron density. However, steric factors, due to the large size of the triphenylphosphine group compared to carbon monoxide will also have some effect.

The cycloheptatrienyl chromium tricarbonyl cation, $[C_7H_7Cr(CO)_3]^+$ will react with nucleophiles to form the 7-exo substituted cycloheptatriene complex [8][19], while the analagous molybdenum cation, rarely forms complexes such as [8] but instead undergoes nucleophilic attack at the metal. Thus, $[C_7H_7Mo(CO)_3]^+$ reacts with NaI in acetone to form the neutral species $C_7H_7Mo(CO)_3I$ [19]. This suggests that while for chromium the positive charge resides mainly on the ring, in the case of molybdenum it resides largely on the metal atom. Some metal-olefin complexes undergo ligand exchange by an S_N2 reaction. This mechanism occurs in the rapid exchange reaction which takes place between free ethylene and ethylene co-ordinated to the square planar complex, bis(ethylene)rhodium acetylacetonate. Initial reaction is thought to involve donation of electron density from the $2p\pi$ bond of a molecule of free ethylene into a vacant p orbital on the metal forming a five-co-ordinate activated complex. Evidence for this comes firstly from the fact that perdeutero ethylene, (C_2D_4), will exchange with co-ordinated ethylene in bis(ethylene)rhodium acetylacetonate, but not in bis(ethylene) rhodium cyclopentadienyl[27] which has two more electrons, giving it an inert gas configuration and leaving no vacant orbitals to receive charge from the incoming olefin, and secondly from the fact that although tetrafluoroethylene forms a much more stable complex with rhodium than ethylene, it reacts far more slowly with bis(ethylene)rhodium acetylacetonate than does ethylene itself[12], suggesting that the electron-withdrawing effect of the fluorine atoms reduces the charge density between the two carbon atoms so making the molecule a poorer nucleophile and reducing the rate of formation of the activated complex.

Nucleophilic attack on free benzene is relatively rare, but arenes



[SCHEME 3]

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO$$

[9]

co-ordinated to a metal have enhanced reactivity towards nucleophiles[28]. Thus base catalysed deuteration of benzene chromium tricarbonyl proceeds far more rapidly than for benzene[29] and $C_6H_6Cr(CO)_3$ reacts readily with sodium methoxide to form $(C_6H_5OMe)Cr(CO)_3$[28].

Hydrogen Transfer

Many isomerisation reactions of olefins which will not occur in the free state, take place readily when the olefin is complexed to a transition metal, and it is clear that many of the reactions of this type involve transfer of a hydrogen atom from the olefin to the metal and then back to a different site on the olefin. Thus certain hydrogen atoms on the olefin are labilized by the metal, those most affected generally being in the β position with respect to the metal, [SCHEME 2] illustrates a hydrogen transfer involving a 1-3 hydrogen shift. If the metal complex is already in the form of a hydride then an alternative method involving a 1-2 shift is possible, [SCHEME 3][30].

The course of any isomerisation reaction is often very difficult to predict. Many of the reactions occur with great ease and under very mild conditions. Obviously relative thermodynamic stabilities of the isomers are important, but other factors, such as the steric effects that olefin substituents would have on the metal, and the number of electrons which the metal is willing to accept from the ligand will also control the course of the reaction. Not only are the relative thermodynamic stabilities of the free olefins important but also those of the complexed olefins. Cyclo-octa-1,3-diene, being a conjugated diene is thermodynamically more stable than cyclo-octa-1,5-diene. These two, together with the 1,4 isomer, are readily interconverted by aqueous rhodium trichloride. However, cyclo-octa-1,5-diene is the only one which forms a stable complex with the rhodium compound. Therefore, when cyclo-octa-1,3-diene is added to an aqueous solution of rhodium trichloride, it forms the stable 1,5 complex, from which free cyclo-octa-1,5-diene can be recovered[30]. Hence, in this case, it is the stability of the complex rather than the free olefin which is important.

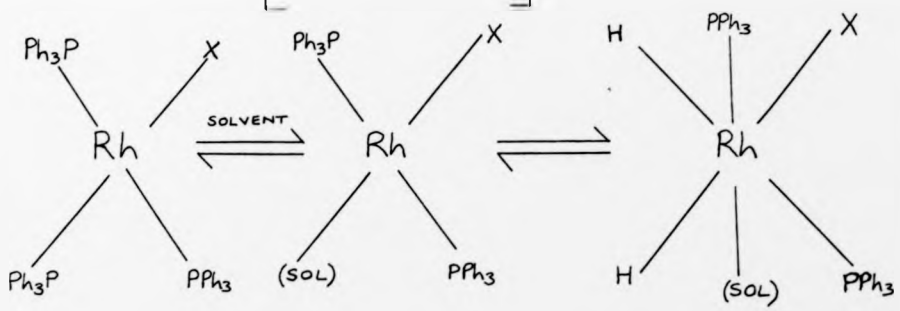
a) $Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$

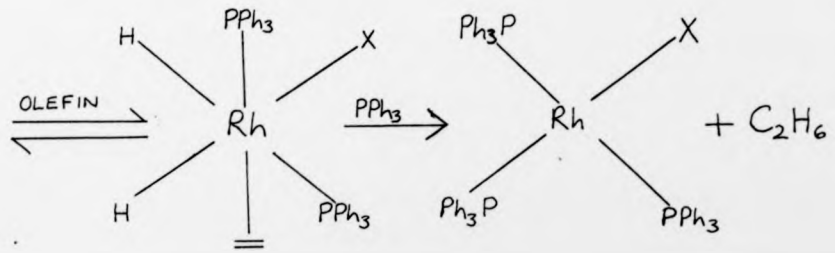
$HCo(CO)_4 + RCH{=}CH_2 \rightleftharpoons (RCH{=}CH_2)HCo(CO)_4 \rightleftharpoons (RCH_2CH_2)Co(CO)_4$

b) $(RCH_2CH_2)Co(CO)_4 + CO \rightleftharpoons (RCH_2CH_2CO)Co(CO)_4$

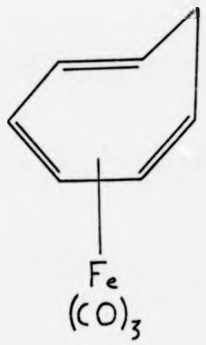
$(RCH_2CH_2CO)Co(CO)_4 + HCo(CO)_4 \longrightarrow RCH_2CH_2CHO + Co(CO)_8$

[SCHEME 4]

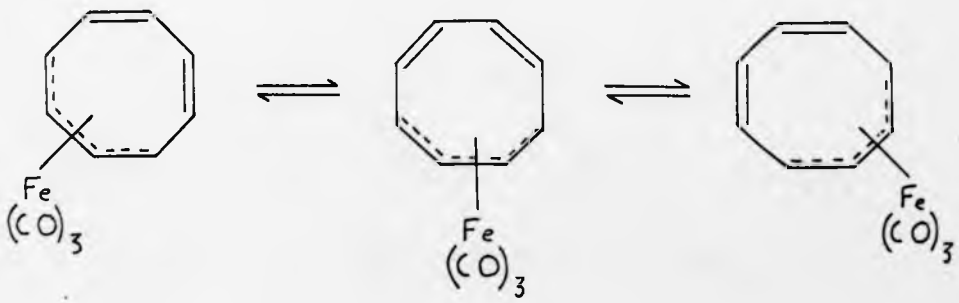




[SCHEME 5]



[10]



[SCHEME 6]

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Reactions involving transfer of hydrogen from a metal atom to an olefin also form an important step in many industrial processes which utilize transition metal compounds as catalysts. One example of this is the hydroformylation or 'OXO' process [9]. The active catalyst in this reaction is $HCo(CO)_4$, formed from $Co_2(CO)_8$ and H_2, and the reaction involves two basic steps [SCHEME 4][31].

Metal catalysed hydrogenation of olefins also often involves a hydrogen transfer step from the metal to the olefin. In [SCHEME 5], involving tris (triphenylphosphine) rhodium halide as catalyst, the hydrogen is first activated by forming a cis-dihydride with the solvated rhodium compound, followed by displacement of the solvent molecule by the olefin and transfer of the bonded hydrogens to the olefin.

The olefin only forms a weak association with the metal, as can be seen from the fact that, if it is a strong π acid, and therefore capable of accepting charge from, and so forming a strong bond with, the metal, then hydrogenation does not occur[32]. Thus, in cycloheptatriene iron tricarbonyl [10], in which two of the double bonds are firmly bound to the metal, catalytic hydrogenation only occurs at the free double bond. Cyclooctatetraene iron tricarbonyl, $(C_8H_8)Fe(CO)_3$, does not undergo hydrogenation at all. This appears to suggest that all four double bonds are strongly bonded to the iron. Apart from the fact that this is an unsatisfactory explanation from an electronic viewpoint, it is not acceptable in the light of the fact that two of the double bonds cannot be firmly bonded to iron, since they react with the dienophile, tetracyanoethylene in a Diels Alder addition. The mode of bonding in this compound is therefore considered as valence tautomerisation or 'ring whizzing' by means of a 1,2 shift. [SCHEME 6]

Clearly, the mode of bonding between olefins and transition metals alters the electron densities of both, thus affecting their reactivity and/or stability and opens up the possibility of formation of new compounds and new synthetic routes, by making use of intermediates which are not normally stabilised long enough to enable them to react.

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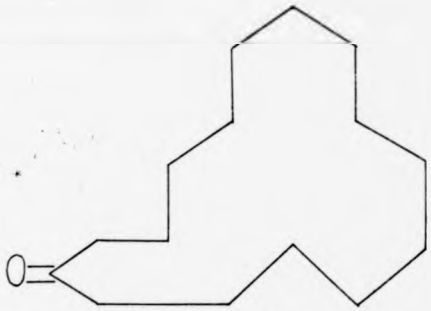
PART ONE



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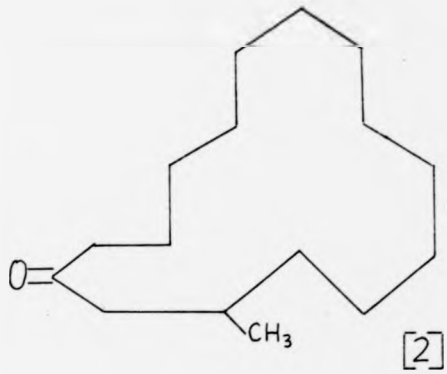

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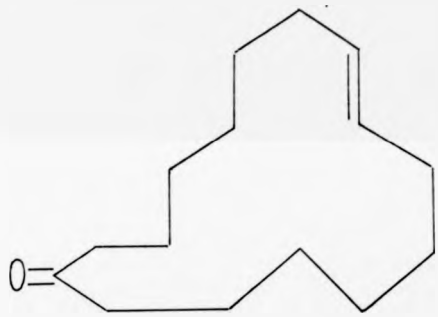

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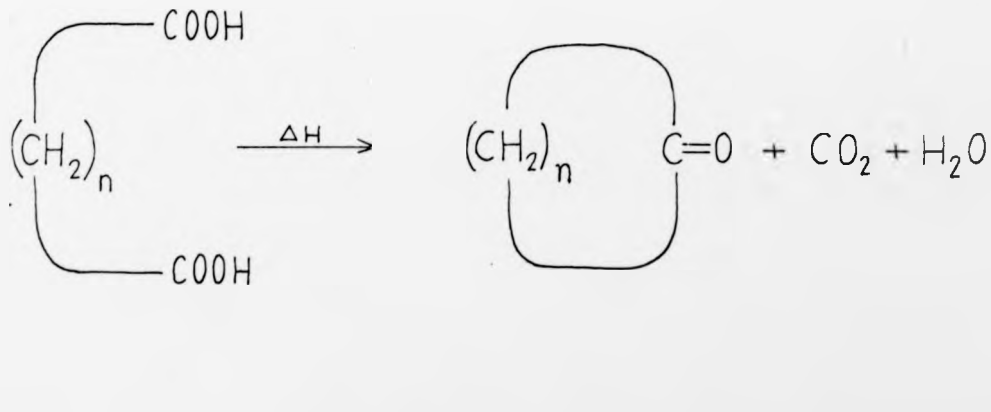

[Eq 1]

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CHAPTER 1

Objective Of Work And Experimental Approach

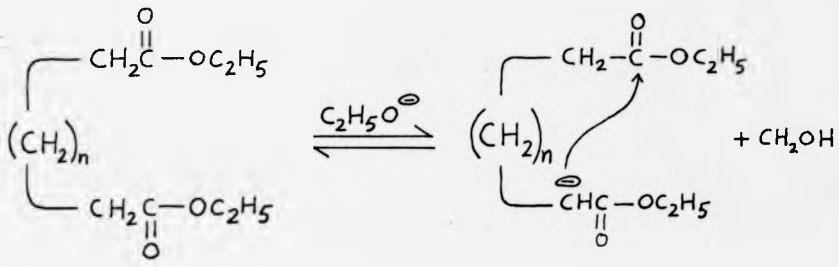
Many large ring compounds from animal sources have a suitable odour for use in the perfume industry. Cyclopentadecanone, (exaltone) [1], its methyl derivative muscone [2] and civetone [3] are examples of fifteen-membered carbocyclic rings which are useful in this way.

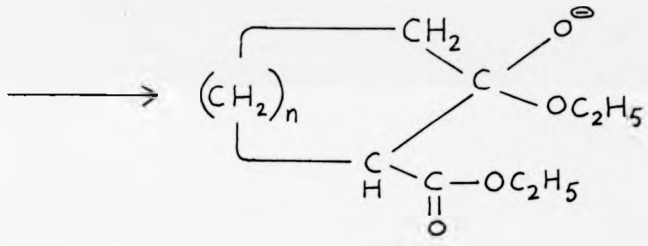
The main disadvantage to the application of these compounds is that they are relatively difficult to obtain from natural sources and therefore expensive. Hence, any synthetic route to this group of compounds is of particular interest.

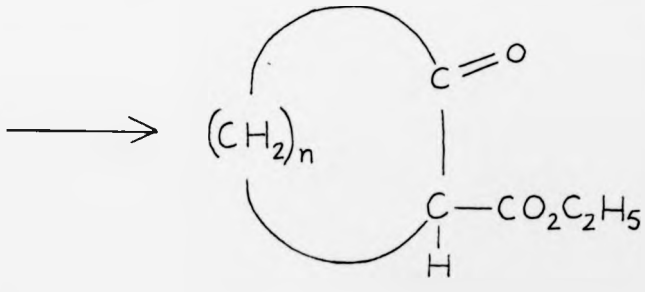
The main problems encountered in synthesis of large ring compounds in general, are that the likelihood of two ends of a chain joining will decrease as the length of the chain increases, (distance factor), and this is coupled with the fact that various non-bonding interactions within the molecule, (steric factors), may tend to keep the two ends of the chain in conformations which are unfavourable to cyclisation. This is particularly noticeable in medium rings, (8-11 carbon atoms), where both the distance factor and the steric factor play an important part in preventing cyclisation, compared with smaller rings where the distance factor is small and larger rings where the steric factor is small. This means that for medium rings the minimum in the yield is cyclisation. While increased chain length adversely affects cyclisation, it also, by the same reasoning, favours intermolecular interactions to produce long chain polymeric compounds, although this can be overcome in certain cases by carrying out the reaction under conditions of high dilution, when intermolecular reactions become less likely. There are several standard cyclisation reactions in which these problems become evident.

The Blanc cyclisation reaction, Eq. 1 , of dicarboxylic acids with at least three carbon atoms between the two carbonyl groups, involves pyrolysis of either the acid or its thorium salt to produce a cyclic ketone. While this reaction is useful for small ring compounds, (cyclohexanone can be prepared in 80% yield), for larger rings the yield drops rapidly, being only 0.5% for cyclodecanone.

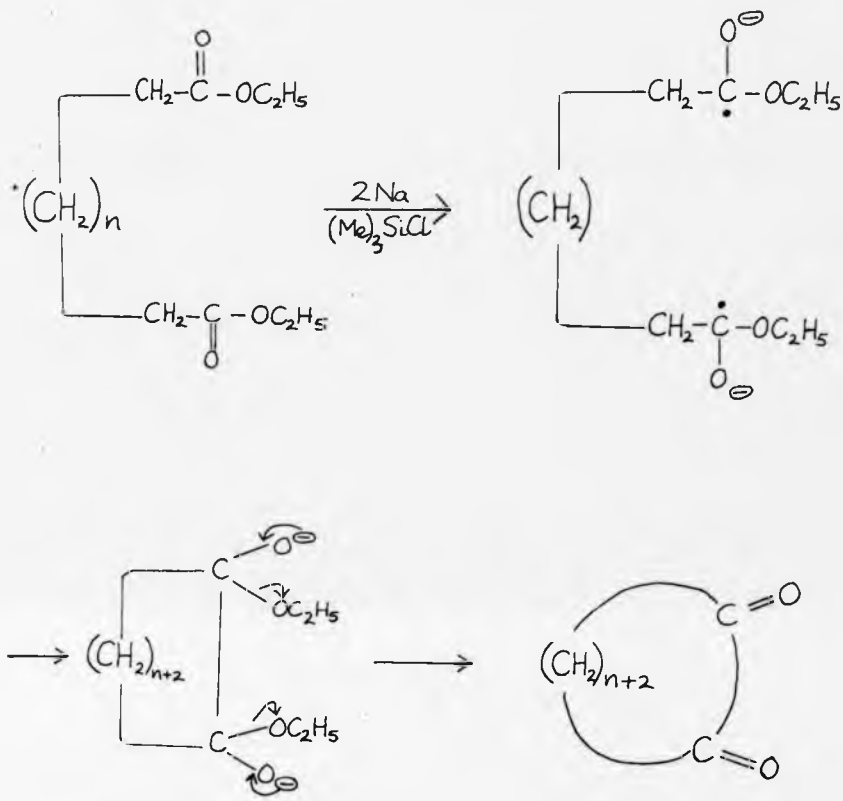
$_2 + H_2O$







[Eq 3]



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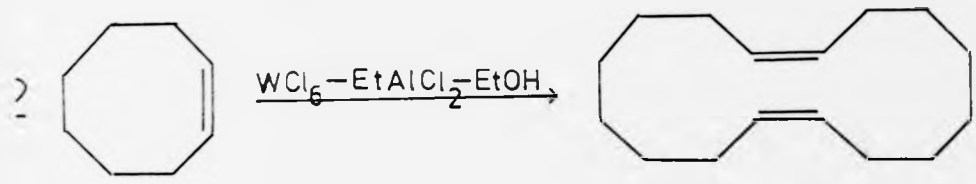
A similar method to the above is the Thorpe reaction, Eq. 2 , involving cyclisation, in the presence of an alkyl lithium compound, of a linear dinitrile to give a cyclic ketone. Again, the yields are poor for larger rings, but in this case they can be considerably improved by the use of high dilution techniques which cuts down intermolecular polymerisation, and gives yields of up to 60% for the C_{14}-C_{25} range.

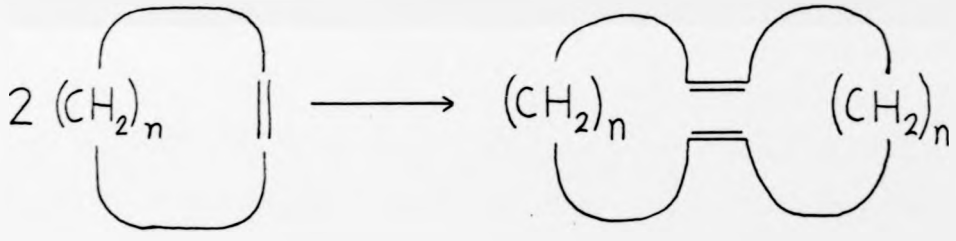
The Dieckmann reaction, Eq. 3 , is also frequently used to obtain cyclic compounds. It is the intramolecular equivalent of the Claisen condensation of two esters and involves abstraction, by ethoxide ion, of a proton from the α methylene group of one of the esters, forming an anion which then attacks a carbonyl group to give the product by loss of ethoxide ion. This reaction also has the disadvantage that although it is carried out in dilute solution, for larger rings yields are still low.

The acyloin condensation, Eq. 4 , while being similar to the Dieckmann reaction, is far more efficient, giving in many cases yields of almost 100% It also involves a diester, but the reagent, instead of being sodium ethoxide in ethanol, is either molten sodium or a dispersion of sodium in a hydrocarbon solvent. This completely changes the course of the reaction as the sodium can no longer function as a base, but instead acts as a one electron reducing agent and also provides a surface on which the reacting ends of the chain can be brought together, so lowering the entropy of the reaction. A radical anion is formed at each carbonyl group resulting in ring closure followed by elimination of two ethoxide ions. Further reduction then occurs to produce a dianion which, on addition of water, gives the acyloin. There is a danger that ethoxide ions formed during the course of reaction may induce a competing Dieckmann reaction and to avoid this, trimethylsilyl chloride is added to the reaction mixture as a trapping agent.

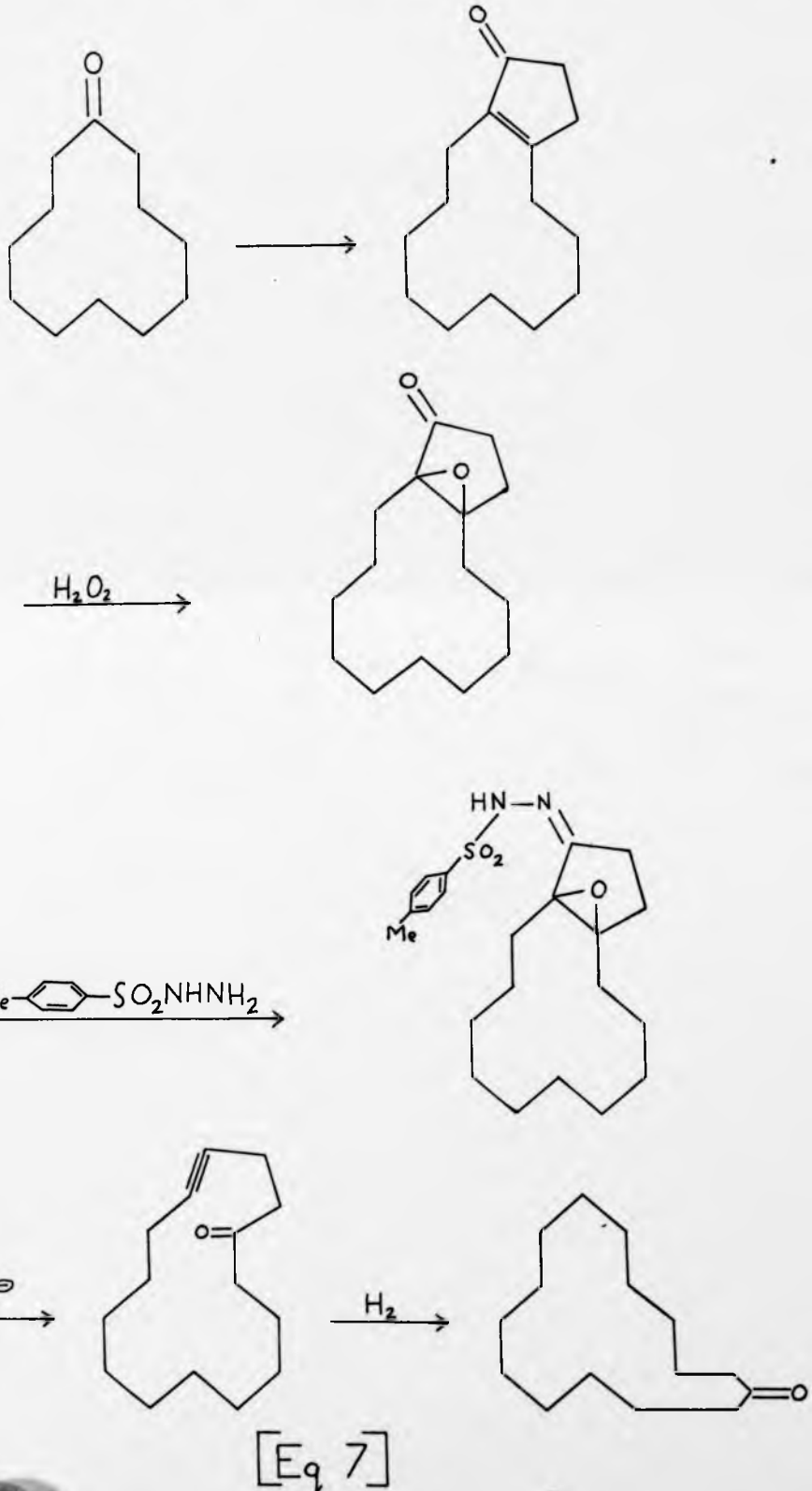
Although the acyloin reaction provides a useful and efficient synthetic route to large ring compounds, especially C_{15} perfume bases, it has the disadvantage that the straight chain precursors for the reaction are almost as difficult and expensive to obtain as are the naturally occuring products.



[Eq 5]



[Eq 6]



[Eq 7]

[Fig 8]

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This has led to a search for a synthetic method for preparing the ring compounds cheaply and easily from readily available starting materials.

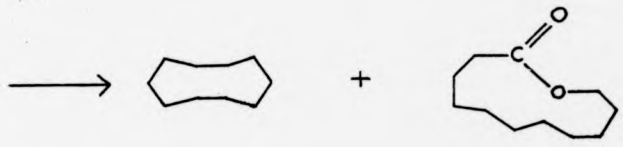
In 1968, Wasserman[1] developed a process for obtaining large ring compounds by treating cyclooctene in benzene, first with tungsten hexachloride and ethanol, followed by ethyl aluminium dichloride under anhydrous conditions, the reaction proceeding via a cyclobutane intermediate, Eq.5 . The trimers and tetramers for this reaction, containing three and four double bonds respectively, were also obtained.

The reaction was then extended to other cyclic monoenes giving the general reaction, Eq.6 .

An interesting approach to the synthesis of fifteen-membered ring ketones involves a fragmentation method developed by Eschenmoser[2]. Cyclododecane, which is readily available, can be converted by a condensation reaction into an α,β unsaturated ketone which is then epoxidised, using hydrogen peroxide, and converted into a p-toluenesulphonyl hydrazone, ($p\text{-}MeC_6H_4SO_2NHNH_2$). This key intermediate, like similar analogues, undergoes fragmentation at room temperature with production of a cyclic acetylene. Simple hydrogenation then gives the fifteen-membered ring ketone in high yield. Eq.7

One of the most successful routes evolved is that due to Story[3], which involves the thermal or photochemical decomposition of ketone peroxides to form carbocyclic hydrocarbons and macrocyclic lactones, Eq.8 The thermal reaction is preferred to the photochemical as it is safer and also gives higher yields and faster reaction times.

The mechanism for this reaction is thought to involve initial homolytic fission of an oxygen-oxygen bond, followed by double β fission resulting in elimination of molecules of carbon dioxide and collapse of the



[Eq 9]

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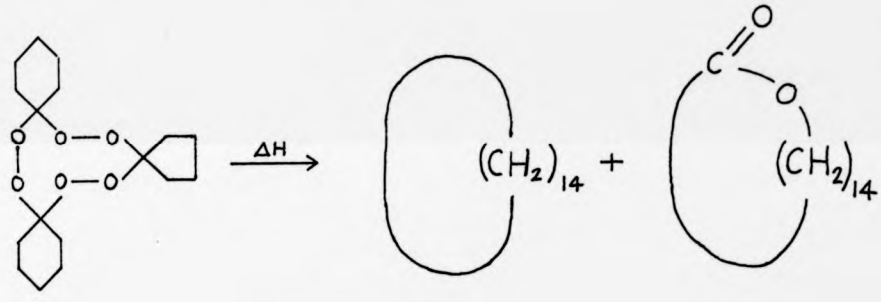

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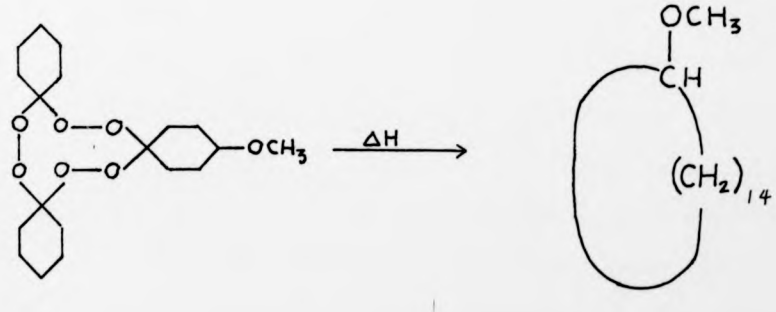
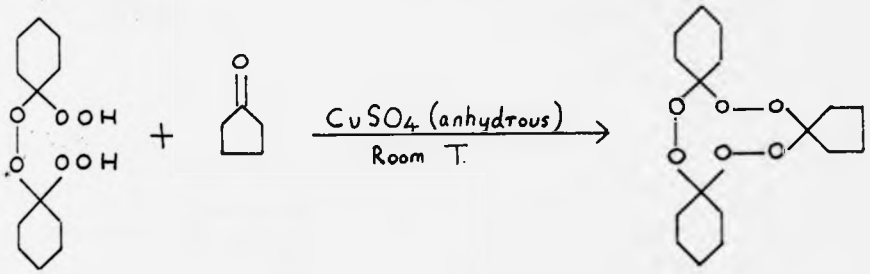
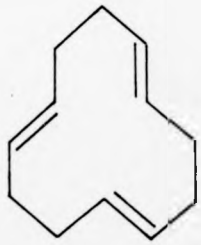


[Eq 10]



[Eq 11]



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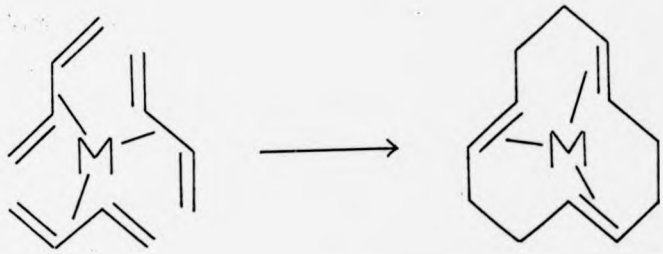
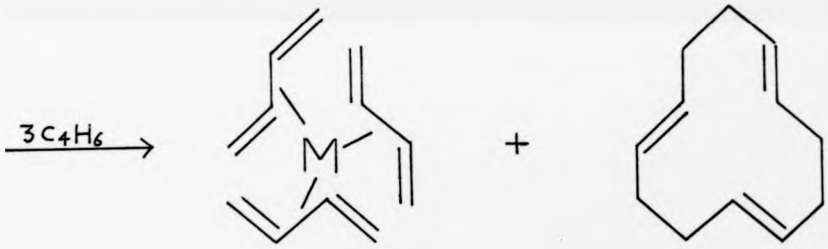
remaining hydrocarbon radicals into the cyclic product, Eq.9 . The formation of the lactones is probably due to radical attack on a molecule of carbon dioxide, followed by cyclisation. By using unsymmetrical and substituted peroxides, the number of possible products is almost unlimited, Eq.10 . One of the main advantages of this reaction scheme is that the starting materials are readily available at reasonable cost. The key intermediate in the synthesis of the trimeric peroxides is 1,1- dihydroperoxydicyclohexyl peroxide, which is reacted with an appropriate ketone, Eq.11 . However, one of the disadvantages of this technique is that peroxides tend to be unstable and therefore are not really suitable for use as intermediates in large scale industrial reactions.

In 1955 Ziegler[4] discovered that a catalyst prepared from tetrabutyl titanate and triethyl aluminium would polymerise ethylene. This led Wilke to investigate the effects of this type of catalyst on the butadiene system[5]. He found that the reaction of butadiene with titanium tetrachloride and diethyl aluminium chloride gave, as the sole product of reaction, cis,trans, trans-1,5,9-cyclododecatriene [4]. Either the presence of the catalyst overcame the forces which normally oppose medium ring formation, i.e. competing intermolecular bond formation to give long chain polymers, or alternatively, because of the particular mechanism of the reaction, these forces did not operate during ring formation. It is interesting that, while most processes for the formation of medium and large ring compounds involve the use of high dilution techniques, this particular reaction occurs normally at high concentrations of butadiene, (in fact, as will be seen, using other transition metal catalysts the reaction may be carried out in liquid butadiene).

One possible mechanism for this reaction is that the transition metal, which is in a low valence state, will attempt to attain the





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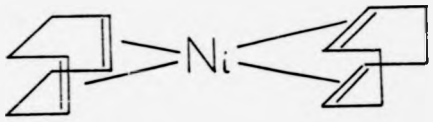
NOTE 1 It will obey the 'eighteen electron rule' which states that organometallic transition metal complexes will tend to have eighteen electrons in the valence shell of the metal, as this, being the electronic configuration for a noble gas, will be favoured both thermodynamically and kinetically. It is particularly valid in the middle of a transition series where the ns, np, (n-1)d orbitals are similar in energy and so contribute equally to bonding. It becomes less valid at the beginning of a series, or in high oxidation states, where the energy of the (n-1)d orbitals is high compared with the ns and np and also at the end of the series where the d orbitals enter the core and the separation between s and p orbitals becomes large.



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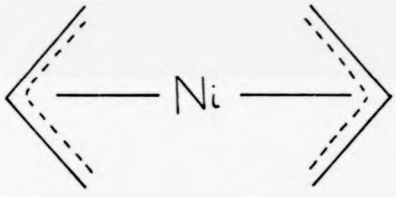

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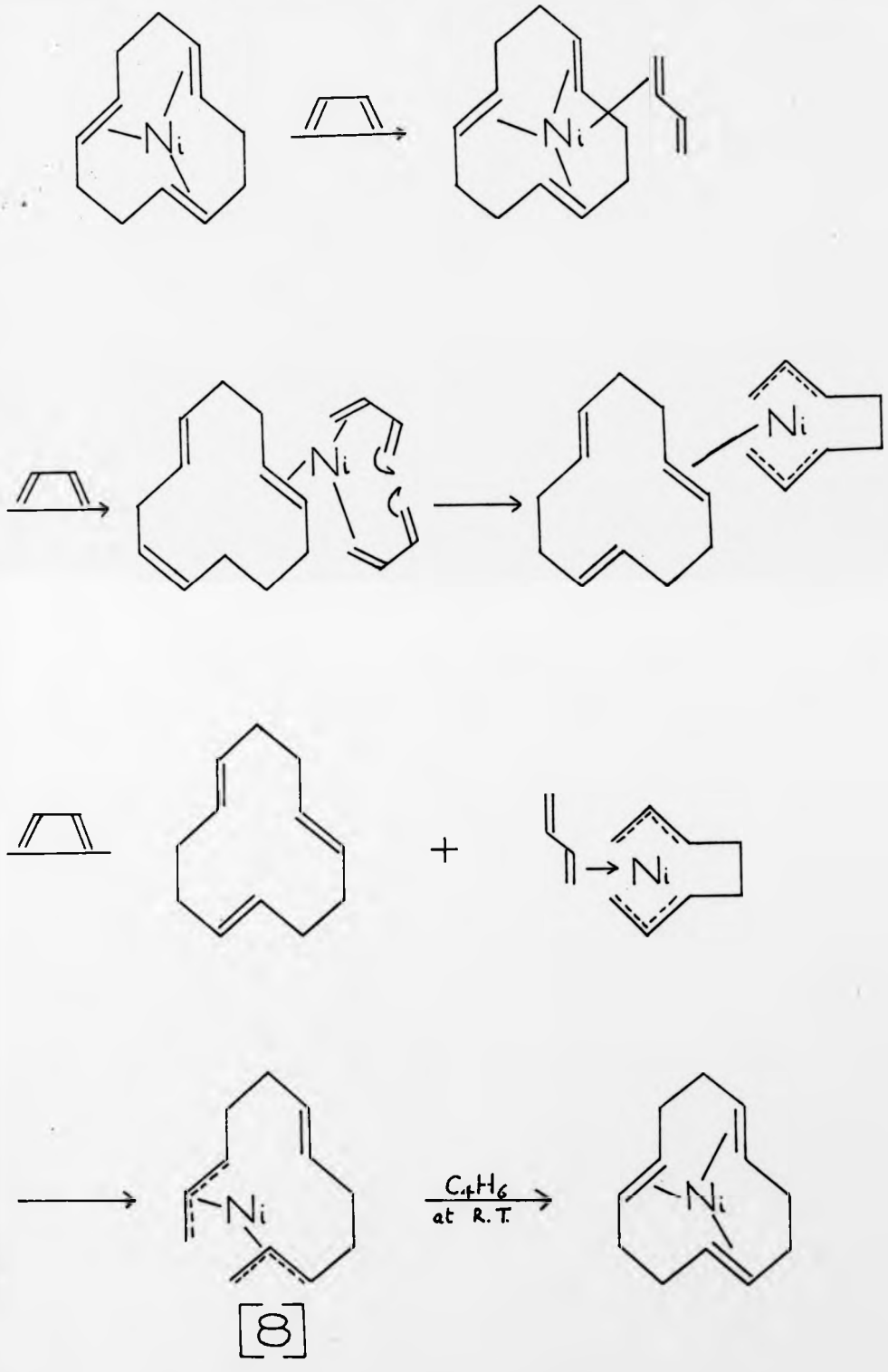

[8]

[Eq 13]

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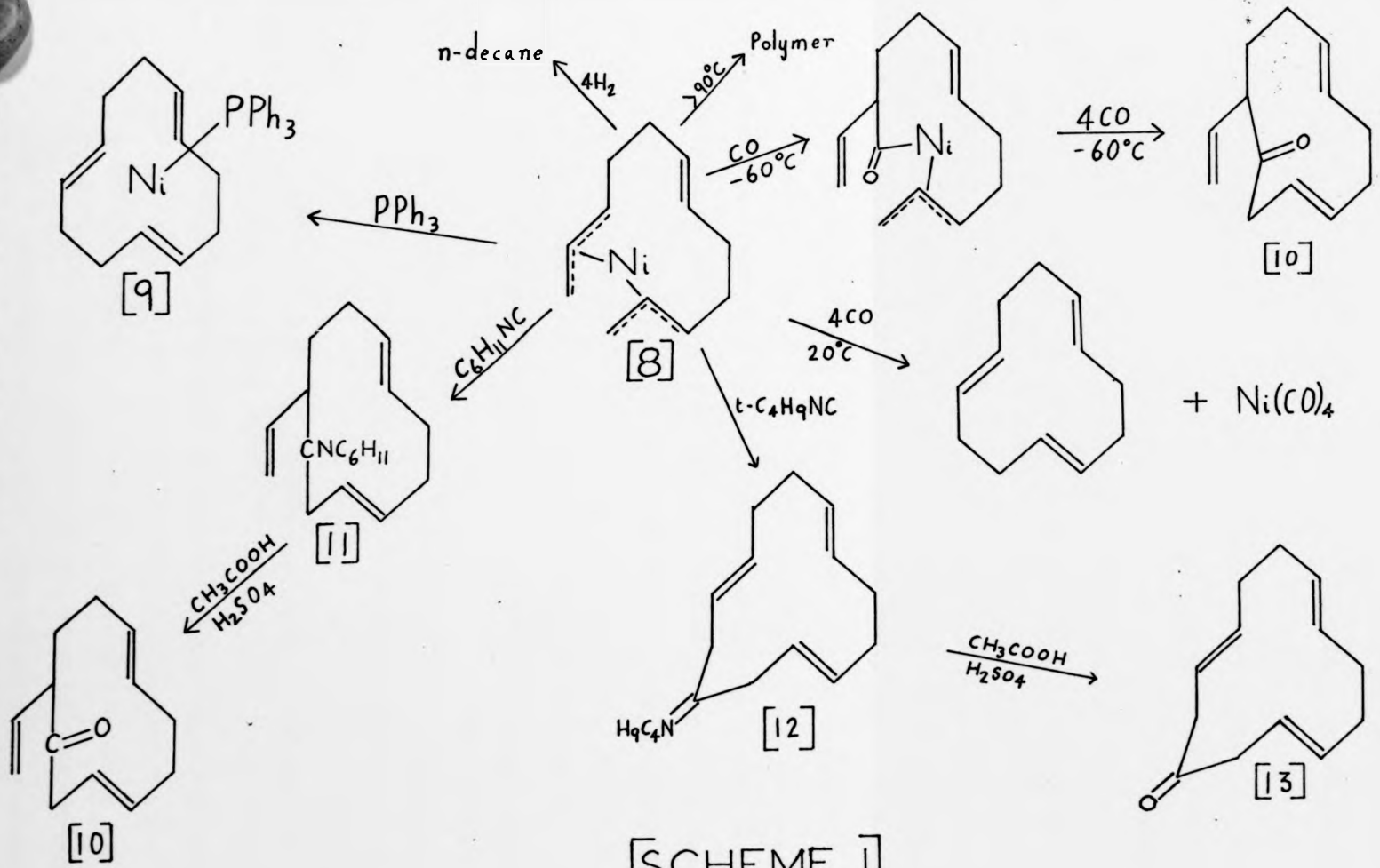
monoxide being

Most of the work on this system has been carried out by G. Wilke and co-workers using Ni(0) as the transition metal.[6]

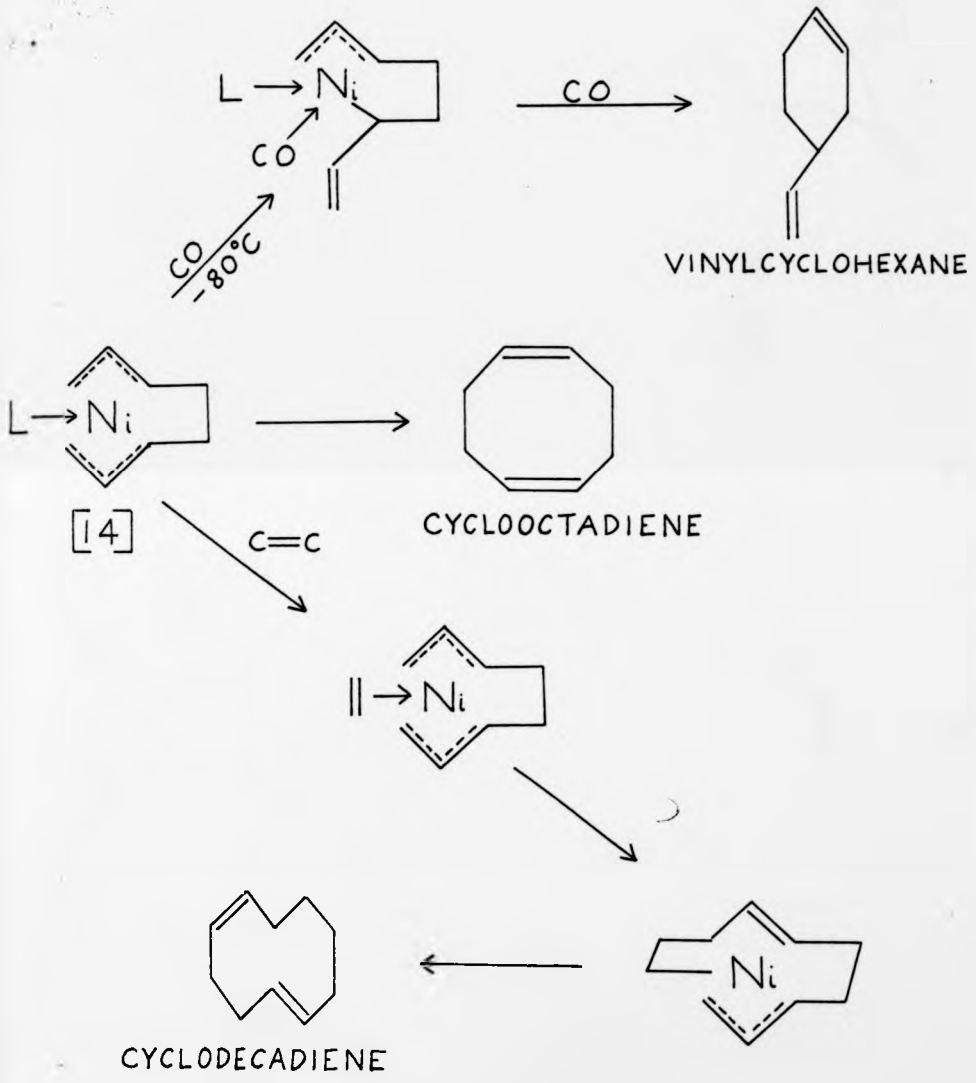
The catalytic production of cyclododocatriene can be achieved using a wide range of organo-nickel compounds as starting materials including bis(cyclooctadiene) nickel, [5], bis-π-allyl nickel, [6] and cyclododecatriene nickel, [7]. In each case, production of cyclododecatriene involves reacting the starting material with excess butadiene at 20°C. Since the function of the starting material is simply to provide a suitably activated nickel atom, its nature does not affect the reaction mechanism, the organic part of the molecule being displaced by butadiene in the first steps of the reaction. This is then followed by stepwise trimerisation, ring closure and subsequent displacement of the trimer by more butadiene, Eq.13 . When this reaction was carried out at -40°C Wilke was able to isolate an intermediate complex $C_{12}H_{18}Ni$, dodeca-2,6,10-triene-1,12-diyl nickel, [8], which was of great use in elucidating the mechanism of the above reaction. [8] is stable at room temperature but on further heating it decomposes to give cyclododecatriene and metallic nickel. It can be converted to CDT by treatment with electron donors such as carbon monoxide, phosphines or even more butadiene. It is the reaction with butadiene and other olefins which gives the system its catalylic property.

The reaction with phosphines [7] under mild conditions causes ring closure and the formation of cyclododecatriene nickel phosphine adduct [9].

The reactions of the intermediate complex, [8], with carbon monoxide [7] and also isocyanides [8], are of particular interest. The reaction with carbon monoxide can take two courses depending on temperature. At 20°C the carbon monoxide causes ring closure followed by displacement of the ring to yield cyclododecatriene and nickel carbonyl. At -60°C the reaction takes a different course, with a molecule of carbon monoxide being inserted between C_1 and C_{10} of the bis-π-allyl to yield


n-decane
4H2
>90°C
Polymer
PPh3
Ni
[9]
PPh3
CO
-60°C
Ni
O
4CO
-60°C
O
[10]
Ni
[8]
C6H11NC
CNC6H11
[11]
4CO
20°C
+ Ni(CO)4
t-C4H9NC
CH3COOH
H2SO4
C=O
[10]
H9C4N
[12]
CH3COOH
H2SO4
O
[13]

[SCHEME I]



[SCHEME 2]

the C_{11} ring syst

The reactio

depending not on

nitrogen. If the

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However, if the

then instead of

occurs between C

Both [11]

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ketones, [10] an

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Wilke foun

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isolated from th

^{1}H N.M.R.

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This is in contr

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If the rea

major product is

the presence of

γ-allyl-σ-allyl

vinylcyclohexene

Reaction

nickel catalyst

the C_{11} ring system, [10].

The reaction with isocyonide can also take one of two courses, depending not on temperature but on the size of the group attached to nitrogen. If the group is cyclohexyl then the reaction is analogous to the insertion reaction of carbon monoxide and [11] is formed. However, if the reagent is the more bulky tertiary butyl isocyanide, then instead of insertion occuring between positions C_1 and C_{10}, it occurs between C_1 and C_{12} to give rise to a C_{13} ring compound, [12].

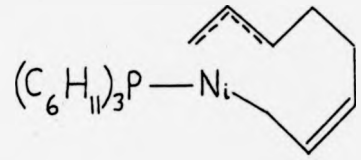
Both [11] and [12] can be readily hydrolysed by a 1:1 mixture of 30% acetic acid and 3.5N sulphuric acid to give the corresponding ketones, [10] and [13]. Thus it would appear that 1,10 addition is favoured over 1,12, the latter occuring when the 10 position is unapproachable due to the size of the incoming group.

Wilke found that if, during the catalytic reaction, a phosphate group such as triphenyl phosphine were present to act as a Lewis base, then instead of trimerisation, dimerisation occured to give cyclooctadiene. This is believed[9] to be due to the presence of an α,ω-octadienediyl-nickel intermediate [14], and indeed, such intermediates have been isolated from the reaction[10,11,12].

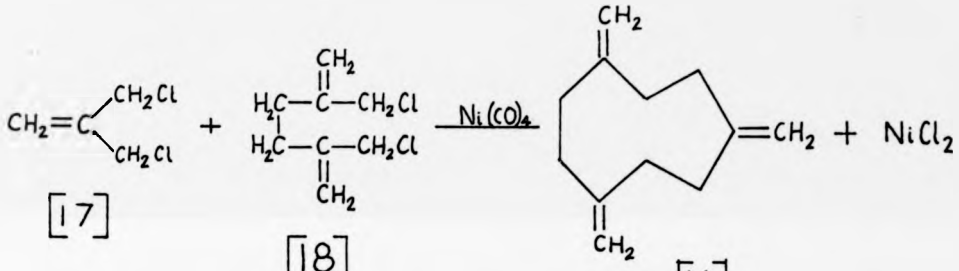
^{1}H N.M.R. studies on [14] with triphenylphosphine as ligand [12] have shown the intermediate to be a symmetrical bis-π-allyl C_8 chain. This is in contrast to ^{1}H N.M.R. studies on the tricyclohexylphosphine analogue [11] which indicate a π-allyl-σ-allyl arrangement, [15].

If the reaction mixture is treated with carbon monoxide, the major product is not cyclooctadiene but vinylcyclohexene. Presumably, the presence of carbonmonoxide leads to preferential formation of the π-allyl-σ-allyl intermediate species, followed by ring closure to form vinylcyclohexene.

Reaction of butadiene with ethylene in the presence of a zerovalent nickel catalyst results in formation of cyclodecadiene [13] and this

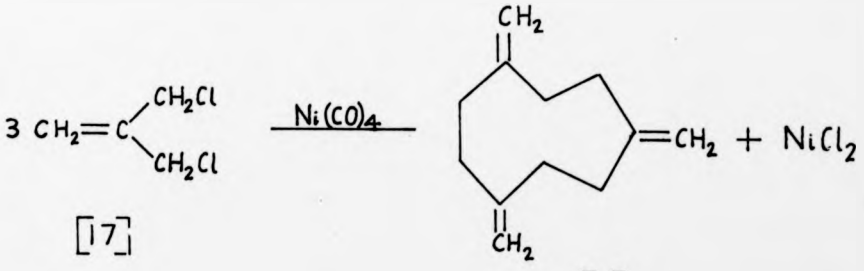


[15]



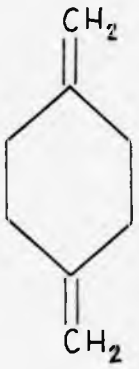
[17] [18] [16]

[Eq 15]



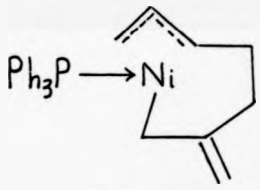
[17] [16]

[Eq 14]

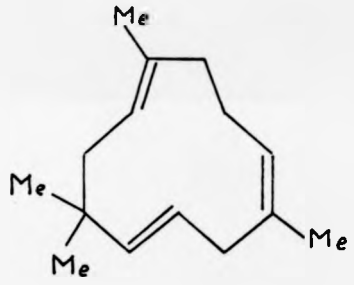


[19]

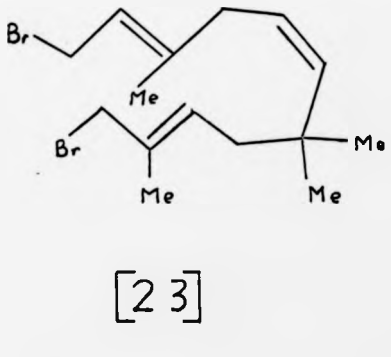
[20]



[21]



[22]



[23]

reaction is also thought to proceed via an intermediate similar to [14], (see Scheme 2).

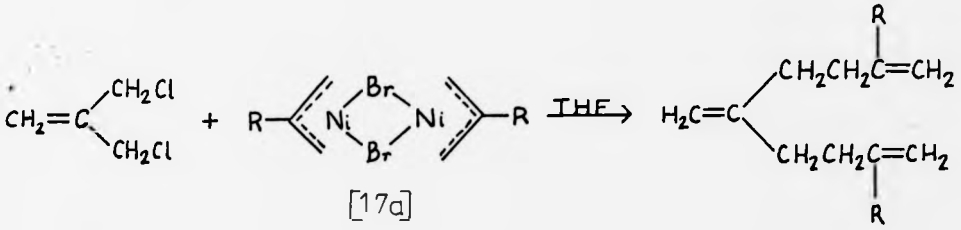
Thus, Wilke has succeeded in producing in fairly high yield, medium and large rings containing six, eight, ten, eleven, twelve and thirteen carbon atoms.

Of particular interest were the eleven and thirteen-membered ring ketones produced by insertion in the bis-γ-allyl intermediate [8]. It was felt that if a carbonyl group could be added across the ends of the two π-allyl groups in [8] to produce [13], then it might also be possible to add a 3 carbon group in the same way to produce a fifteen-membered ring ketone, thus providing a relatively simple and inexpensive synthetic route to the musk-type compounds mentioned earlier.

Corey [14] has described a one step synthesis of 1,4,7-trimethylene cyclononane [16] from 1,1-bischloromethylethylene [17] and nickel carbonyl, in which the nickel carbonyl removes the halogen from the allylic dihalide and so allows cyclisation and coupling Eq.14 .

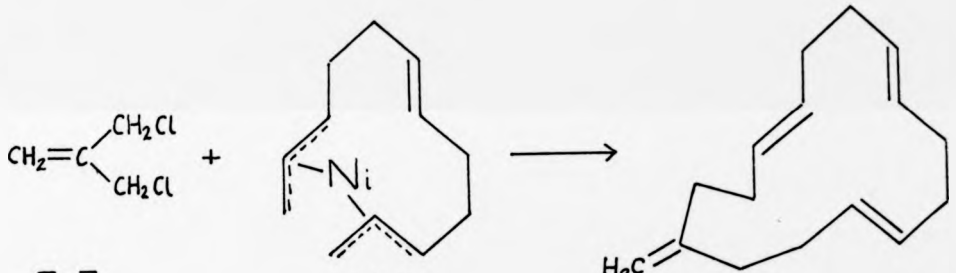
In investigating this reaction, he showed that [16] could also be formed by a coupling reaction between [17] and 1,6-dichloro-2,5-dimethylene-hexane [18], - Eq.15 . He suggests that the intermediates in these reactions are γ-allyl nickel complexes and gives some evidence for this by showing that if, instead of nickel carbonyl, nickel tricarbonyltriphenylphosphine, [$Ni(CO)_3(PPh_3)$], is used, then the product of the reaction is the C_9 compound, 1,4-dimethylenecyclohexane, [19], rather than [16]. This is what one might expect if the reaction intermediate were the bis-γ-allyl complex, [20], since triphenylphosphine would promote formation of the σ,γ-allyl [21], and the dimethylenecyclohexane could then be formed from this by ring closure.

The key cyclisation step in Corey's important work [15] on the total synthesis of humulene, [22], in which the 1,11 dibromo-2,5,9-undecatriene



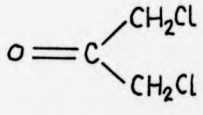
[17a]

[Eq 16]

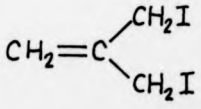


[17] [8] [24]

[Eq 17]



[25]



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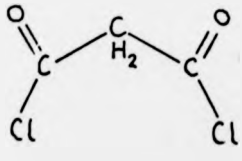
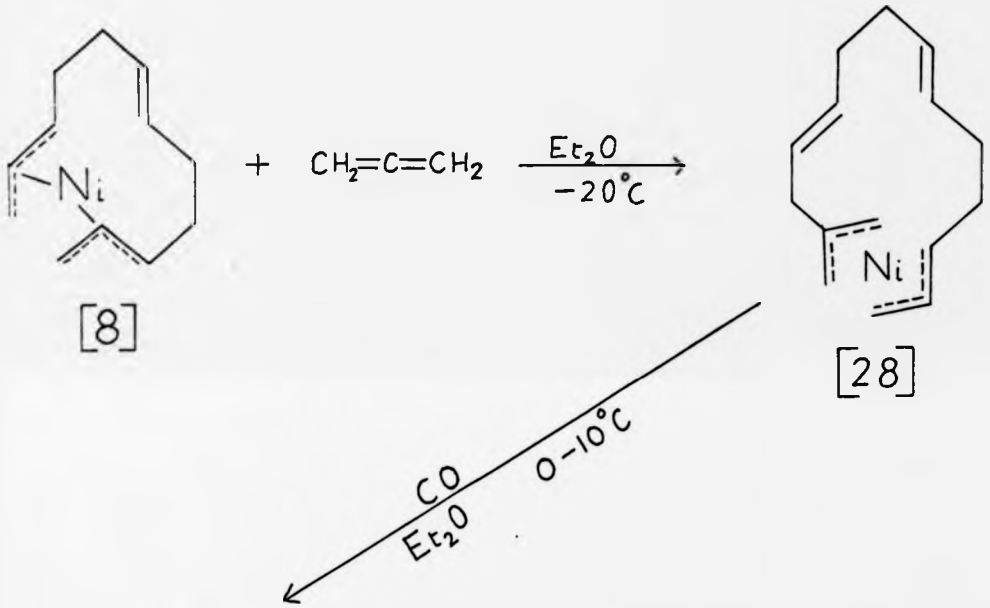
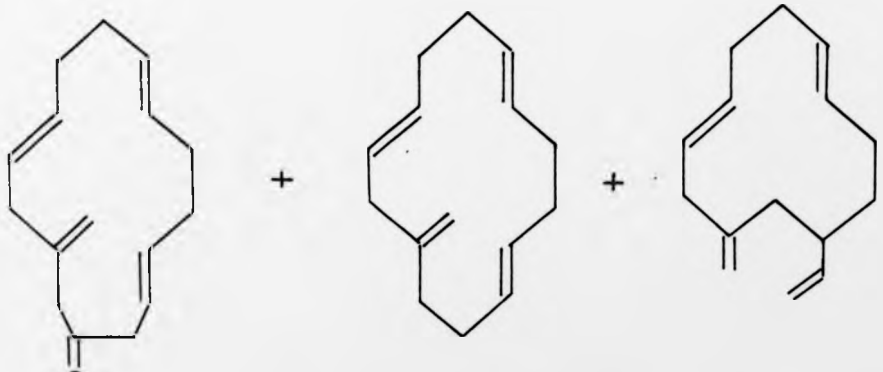


[27]



[8]

[28]



[29]
(4-5%)

MAJOR PRODUCTS

[Eq 18]

derivative, [23], is
is also thought to
bis-π-allyl nickel

Compounds such
also react with bis
the two π-allyl gro

In view of th
which proceeds via
intermediate bis-π
demonstrating the l
that a similar reac
species such as 3-c
a fifteen-membered
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previously mentione
in Eq.17 .

The addition
sym-1,3-dichloroace
3-iodo-2-iodomethyl

It has subse
carbon nickel compl
with a slight exce
reacts with carbon
(4-5%), an unsatur
muscone Eq.16 .

Unfortunatel
time for it to be

derivative, [23], is cyclised in the presence of nickel tetracarbonyl, is also thought to proceed by a similar mechanism involving a bis-π-allyl nickel intermediate.

Compounds such as 3-chloro-2-chloromethylprop-1-ene, [17], will also react with bis-π-allyl complexes of the type [17a], by bridging the two π-allyl groups Eq.16 .

In view of this, and also the cyclotrimerisation reaction of [17] which proceeds via a similar bridging reaction between [17] and the intermediate bis-π-allyl complex [20], together with the work of Wilke demonstrating the lability of the intermediate complex [8], it was felt that a similar reaction might occur between the intermediate [8] and a species such as 3-chloro-2-chloromethylprop-1-ene [17], to give rise to a fifteen-membered ring system [24]. This might be relatively inexpensive to produce and could easily be converted to the musk type compounds previously mentioned. The type of reaction envisaged is illustrated in Eq.17 .

The addition reaction was tried with four different reactants : sym-1,3-dichloroacetone, [25]; 3-chloro-2-chloromethylprop-1-ene [17]; 3-iodo-2-iodomethylprop-1-ene, [26], and malonyl dichloride [27].

It has subsequently been shown [16] that a bis-π-allyl, fifteen carbon nickel complex [28] can be produced by reacting the intermediate [8] with a slight excess of allene in ether at -20 to - 10°C and that [28] reacts with carbon monoxide at 0 - 10°C in ether to give in low yield, (4-5%), an unsaturated cyclic ketone [29] which, on hydrogenation yields muscone Eq.16 .

Unfortunately, this important piece of work was not published in time for it to be of use, but it will be considered again in discussion.

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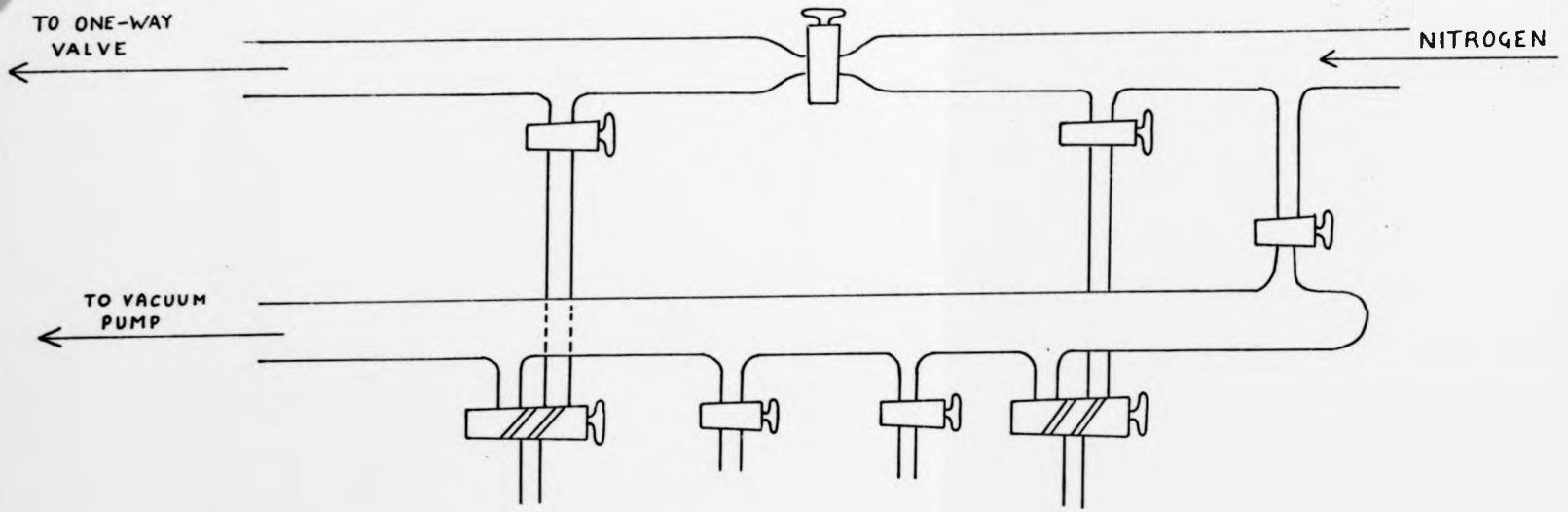
TO ONE-WAY VALVE
NITROGEN
TO VACUUM PUMP

[31]

Some Reactions of

2.1 Preparation

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$(COD)_2$ Ni is use
being produced

CHAPTER 2

Some Reactions of Dodeca-2,6,10-triene-1,12-diyl nickel, 8

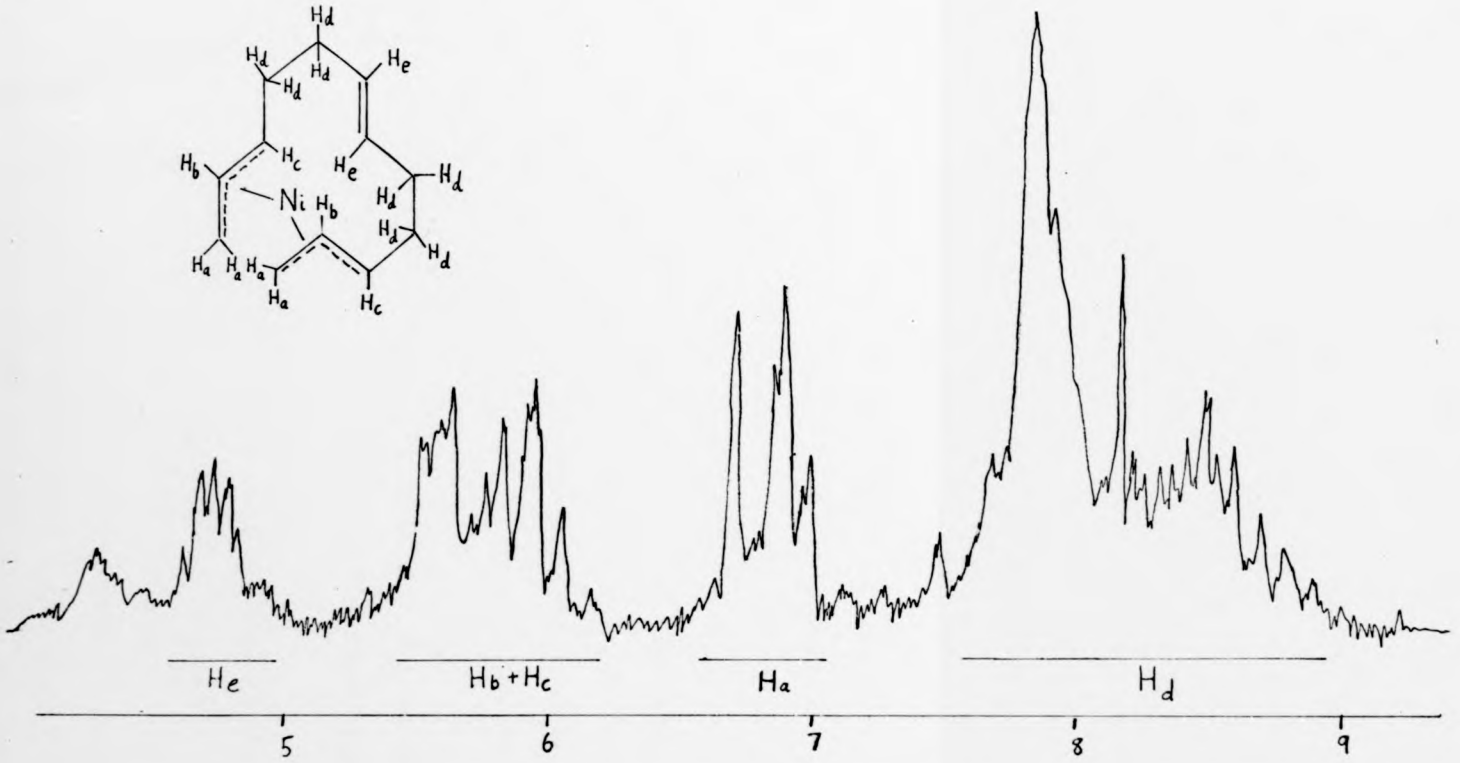
2.1 Preparation and Characterisation of CHTNi, [8]

The initial isolation of a pure sample of dodeca-2,6,10-triene-1,12-diyl nickel was difficult and time consuming as it involved development of techniques for manipulating reactants and products in a completely inert atmosphere. Efficient handling was finally achieved using a vacuum line, [30], in conjunction with schlenk tubes [31] and submerged, positive pressure filtration tubes [31]. Details of the procedure are given in the experimental section.

An initial effort was made to find the most suitable nickel complex from which the bis-π-allyl, [8], could be readily synthesised. This was found to be bis(cyclooctadiene)nickel (0), $(COD)_2Ni$, [5], which can be stored at $-20^{o}C$ under nitrogen, in the solid state for several months. It was prepared by addition of the reducing agent, diethylaluminiumethoxide, to a solution of nickel acetylacetonate, [32], and 1,5-cyclooctadiene, in dry benzene at $0^{o}C$ under nitrogen, and crystallised from the reaction mixture under these conditions.

Trans,trans,trans-cyclododecatriene nickel (0),[7], was also used as a precursor to the intermediate [8]. It was prepared in the same way as the $(COD)_2Ni$ complex, [5], by replacing cycloocta-1,5-diene with cyclododeca-1,5,9-triene in the reaction, under otherwise unaltered conditions.

Whilst [7] does not appear to store as well as [5], (since it is much the more reactive, hence Wilke's description of 'nachte' nickel), it does have the advantage that the only impurity likely to be found in the ultimate product, after filtration, is cyclododecatriene. If $(COD)_2Ni$ is used as precursor, then, in addition to cyclooctadiene being produced in the reaction, there may also be some cyclododeca-


Hd
Hd
Hd
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Hb
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Hb
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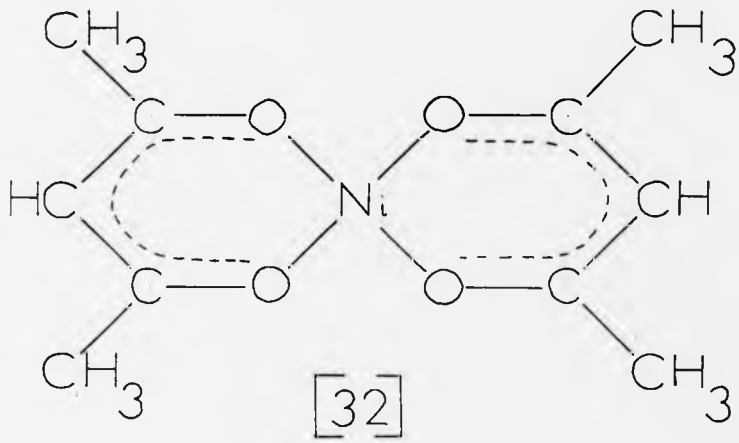
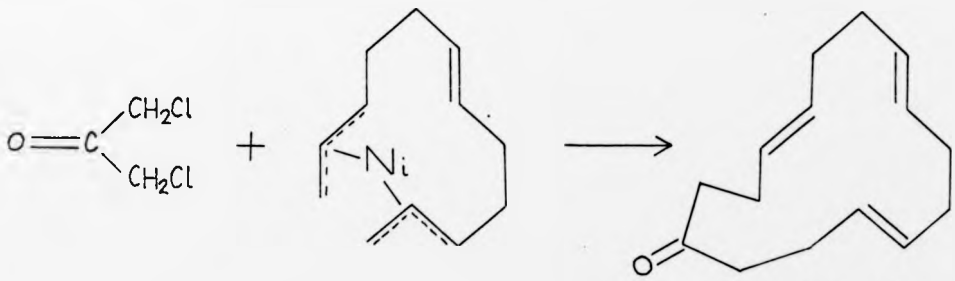
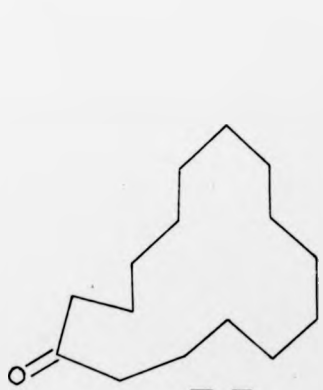


[32]



[34]



[1]

[Eq. 19]

triene formed by
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removed under va
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displacement of
$(COD)_2Ni$, [7], i

Following
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(H_e=4.8τ), H_b r
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2.2 Reaction o

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were successful
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The react
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characteristic

triene formed by ring closure. However, this has to be weighed against the fact that cycloocta-1,5-diene is much more readily removed under vacuum than is cyclododeca-1,5,9-triene, thus making purification easier. So, providing that ring closure and subsequent displacement of cyclododeca-1,5,9-triene can be minimised, then $(COD)_2Ni$, [7], is the better precursor.

Following the method described by Wilke[1], the bis-π-allyl complex, [8], was prepared by dissolving crystalline $(COD)_2Ni$ in liquid butadiene at -40^oC and stirring for several hours, after which the excess butadiene and the displaced COD were removed under vacuum and the deep red solid which remained was recrystallised from pentane. The product was identified by its melting point, (0-1°C), and by its proton N.M.R. spectrum in perdeuterobenzene, [33], which agrees closely with the published 60MHz-^{1}H NMR spectrum of [8][2], despite the fact that it contains traces of unremoved cyclooctadiene and cyclododecatriene.

The spectrum is rather complex, consisting of four broad multiplets due to the large extent of interproton coupling. However, some assignments have been made which are in agreement with the 220MHz-^{1}HNMR and the double resonance studies carried out on this compound[7]. Thus H_e, the protons of the isolated double bond, resonate at lowest field (He=4.8τ), H_b resonate at 5.8τ, H_c at 5.99 and H_a at 6.88τ. The resonances of the aliphatic protons H_d form a broad, complex band centred at 8.05τ, (see fig. [33]).

2.2 Reaction of the Intermediate Complex [8] with Dichloroacetone

This was the most obvious choice for the initial reaction, since if it were successful it would give rise to cyclopentadecatrienone, [34], which would on hydrogenation produce exaltone [1], - see Eq.19 .

The reaction was carried in benzene at 0°C. Chromatography of the product on neutral alumina gave a mobile, pale yellow oil with characteristic odour. It was not possible to completely characterise

IR SPECTRUM		NMR SPECTRUM	
Band cm^{-1}	Remarks	Resonance centered at	Remarks
3490	medium broad	4.6	broad multiplet
1605	medium broad	6.41	sharp singlet
1263	strong	7.95	broad multiplet
1058	strong		
813	medium		
762	medium		
735	medium		

TABLE 1

IR SPECTRUM		NMR SPECTRUM	
Band cm^{-1}	Remarks	Resonance centered at	Remarks
762	medium broad	6.41	sharp singlet
		8.75	broad multiplet

TABLE 2

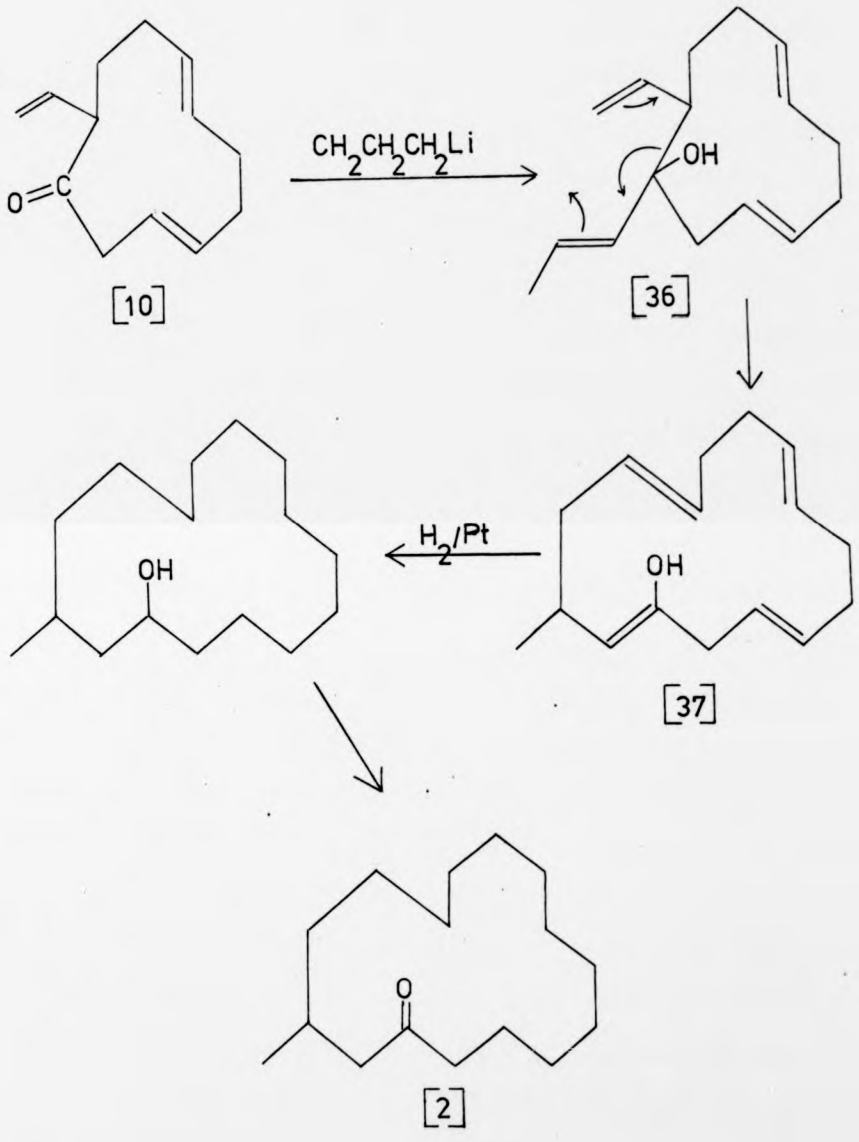
this, although some information as to its nature was obtained using spectroscopic techniques.

Infra-red and ^{1}HNMR spectra of the product were taken and the key details of these are shown in Table 1. The oily product was then hydrogenated to give a white waxy solid and further I.R. and N.M.R. spectra taken, (Table 2).

From Table 1 it can be seen that there is no absorption which can be attributed to a carbonyl group, the only absorption in that region, (1605cm^{-1}), being attributed to olefinic bonds and the presence of these is confirmed by the broad multiplet at 4.6τ in the NMR spectrum. The two fairly strong absorptions at 1263 and 1058cm^{-1} are assigned to carbon/oxygen single bond stretch, and, together with the broad band centred at 3490cm^{-1} suggest the presence of hydroxyl groups. These bands disappear on hydrogenation, which suggests that the alcohol is tertiary or allylic.

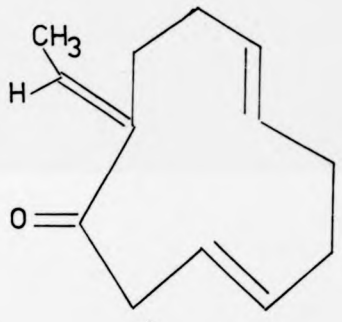
The two medium absorptions at 813 and 735cm^{-1} in the I.R. spectrum, (Table 1) are assigned to olefinic C-H bend, since they disappear on hydrogenation, (see Table 2), whilst that at 762cm^{-1} does not disappear and is assigned to carbon-chlorine stretch. This is confirmed by the presence of the sharp singlet at 6.41τ in both NMR spectra, (See Tables 1 and 2), since methylene protons on a carbon atom attached to chlorine, (i.e. $-CH_2-Cl$), typically resonate at 6.4τ and also the sharp singlet is removed by reduction with lithium in liquid ammonia as would be expected for a halogen group.

It is obvious from the above that the reaction did not proceed as expected and that the desired product was not obtained. It would appear, from the spectroscopic evidence, that one molecule of dichloroacetone has reacted with each end of the bis-π-allyl, [8], to give as the major product a molecule of structure [35]. This suggests that



[10] [36] [37] [2]

[Eq 20]



[38]

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2.3 Reaction of

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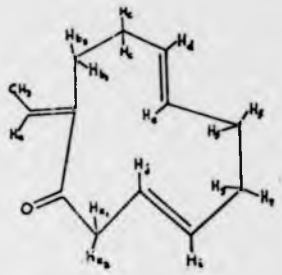
organonickel complexes show a similar reactivity pattern to organolithium compounds or Grignard reagents, preferring to react at the carbonyl centre of an α-halo ketone. This being the case, we decided to study the reaction with other substrates.

2.3 Reaction of the Intermediate [8] with Carbon Monoxide

It has been reported by Wilke[1] that the intermediate complex [8] will react with carbon monoxide at -60°C giving 2-vinylcycloundeca-5,9-dien-1-one, [10]. It was thought that [10] could be reacted with propenyl lithium, (CH_3CH CH Li), undergoing attack at the carbonyl carbon to produce [36]. Subsequent Cope rearrangement would give the fifteen carbon ring, [37], which, on hydrogenation followed by oxidation would yield muscone, [2], (See Eq.20).

Unfortunately this particular reaction was not successful, but in the course of the preparation of the 2-vinylcycloundeca-5,9-dien-1-one, [10], it was discovered that a very facile, specific isomerisation occurred, converting the $\beta\gamma$ unsaturated ketone [10], to the $\alpha\beta$ unsaturated form [38]. An isomeric form of [10] has been previously reported during the preparation by Bogdonovic[2], who suggests that it is a stereoisomer. However, we have now clearly shown that this is not the case and that in fact double bond isomerisation has occurred.

Compound [10] was prepared by bubbling carbon monoxide into a solution of [8] in pentane[2]. After removal of nickel carbonyl and pentane under high vacuum, an infra-red spectrum of the unpurified product was taken, which agreed with the published spectrum of [10], (See [39a]), although since the product was unpurified it also contained some cyclododecatriene. In order to separate the product from cyclododecatriene it was chromatographed on neutral alumina using pentane as eluent. The less polar fraction, apparently homogeneous, was not identical with the main component of crude product, as is clearly shown



[40a]

[40b]

[40c]

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1,3-proto
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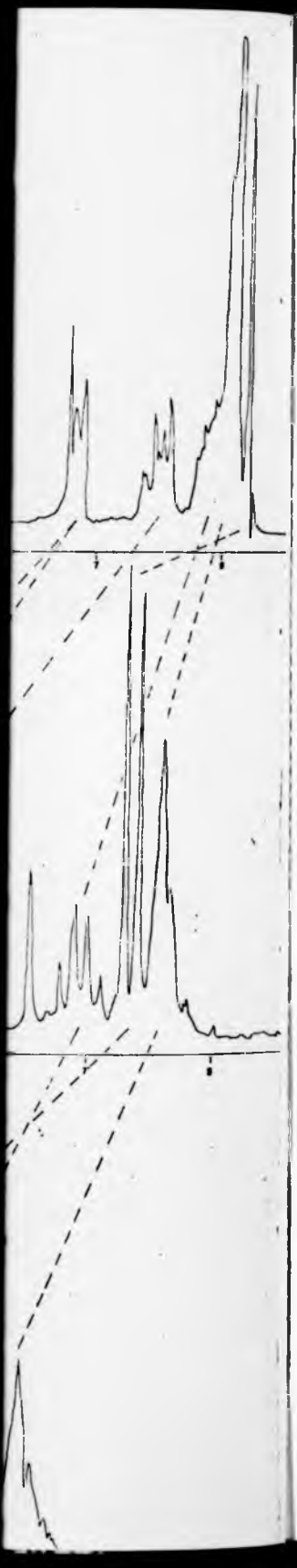


by its infra-red spectrum [39b]. Of particular interest was the carbonyl shift from 1712cm^{-1} to 1665cm^{-1}. An NMR spectrum [40a], of the recovered product, did not agree with the published spectrum[2] of 2-vinylcycloundeca-5,9-dien-1-one, confirming that rearrangement had occurred during chromatography. There is good evidence from both the NMR and IR spectra that the new compound is formed by specific 1,3-prototropic rearrangement of the vinyl group of [10] and that it is the $\alpha\beta$ unsaturated ketone [38].

This deduction is based on four main points:

1. Loss, in [39b], of the absorption of 920cm^{-1} in Fig. [39a] which is due, in the latter spectrum, to the vinyl group.
2. The shifting to lower wavenumber of the carbony absorption, which would be expected for an $\alpha\beta$ unsaturated ketone.
3. In the published NMR spectrum of the 2-vinylcycloundeca-5,9-dien-1-one, Bogdanovic states that the ratio of olefinic to paraffinic protons is 7:11. However, the NMR spectrum of our product, [40a], clearly indicates that the signal intensities of olefinic and paraffinic protons are in the ratio of 5:13.
4. The NMR spectrum, [40a], shows a one proton quartet at 3.54τ, (J=9Hz). Since it is resonating at such low field it is obviously an olefinic proton and the fact that it is a quartet suggests that it is coupled to the three equivalent protons of a methyl group and at the same time precludes its coupling to another olefinic proton. The only way in which this situation can arise is by the structure of the compound being that of [38].

The above evidence, by itself, provides a good basis for assigning structure [38] to the compound, but in order to gain further information, it was decided to try an NMR shift experiment using the europium complex Eu(fod)$_3$ - tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-

octadionato) europium .

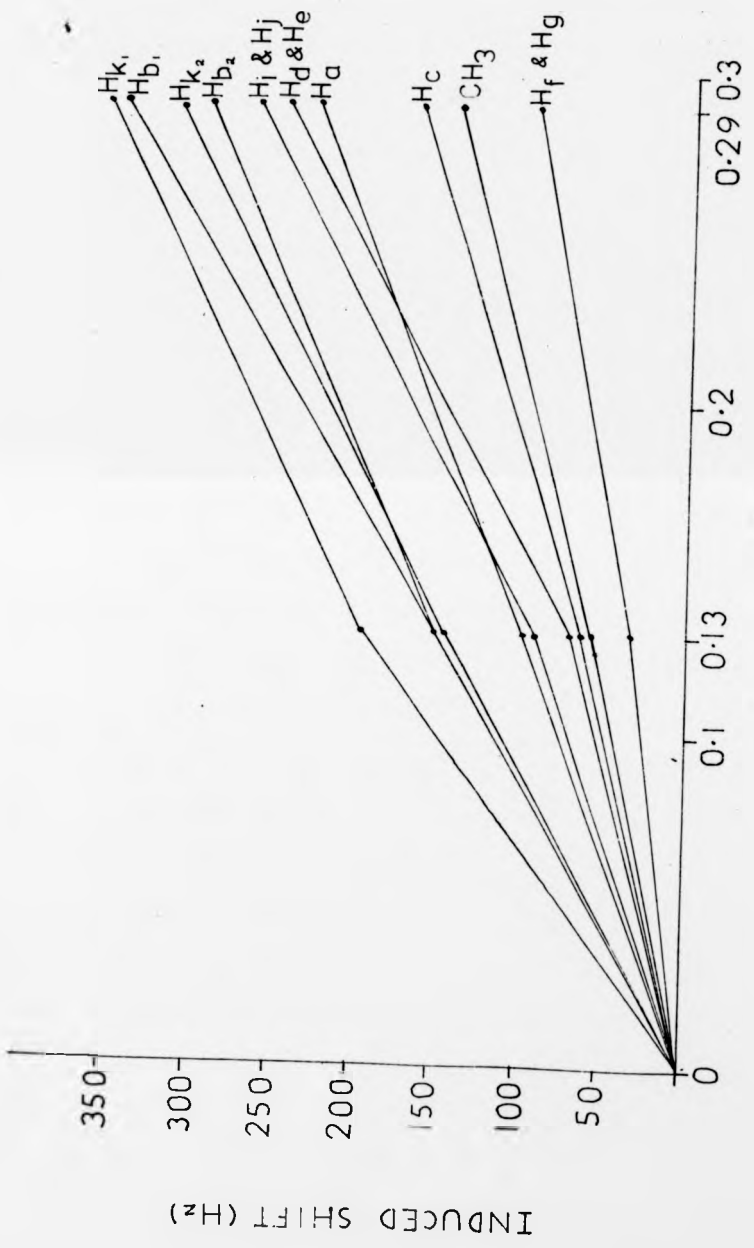
Paramagnetic shifts may arise from two sources; contact or pseudocontact interactions. Contact shifts are dependant on covalent bonding, thus they affect electron density and hence coupling constants. They also cause considerable line broadening in the spectrum.

Lanthanide complexes of polar organic compounds are expected[3] to produce pseudocontact shifts, which are dependant only on distance and geometry, as they arise from magnetic dipolar field effects of unpaired electrons and thus do not affect the bonding electron density. Therefore, using compounds such as $Eu(fod)_3$, paramagnetic shifts can be obtained with minimal broadening and normally with no change of coupling constants since these are field invariant[4].

Pseudocontact paramagnetic shifts are extremely sensitive to the $H\text{-}Eu^{3+}$ distance, $(3\cos^2\theta-1)/r^3$, etc. , the protons closest to the metal ion generally having the greatest shift. Thus, information can be obtained on the relative positions of the hydrogen atoms in the molecule, so giving valuable additional evidence of its structure.

One of the most useful results of this shift experiment is the separation of the aliphatic proton resonances around 8τ in [40a] to reveal a sharp doublet shifted downfield, (7.23τ in [40b] and 5.79τ in [40c]). This is the resonance expected for a methyl group linked to an olefinic carbon atom bearing a single proton and the coupling between this resonance and the one proton quartet at 3.60τ in [40a], (J_{H_a,CH_3}=6cps), confirms that an ($RC{=}CH{-}CH_3$) group is indeed present.

The spectra also indicate that the proton resonances at 7.50τ and 6.82τ in [40a], assigned to H_b and H_k respectively, are split in [40c], suggesting that these protons are diastereotopic due to non planarity of the ring, and slow interconversion of enantiomers at room temperature.


INDUCED SHIFT (Hz)
350
300
250
200
150
100
50
0
0·1
0·13
0·2
0·29
0·3
MOLAR RATIO
H_{k_1}
H_{b_1}
H_{k_2}
H_{b_2}
H_i & H_j
H_d & H_e
H_a
H_c
CH_3
H_f & H_g

[41]

The graph of variation of induced shift with molar ratio $[Eu(fod)_3]/[Ketone]$, fig.[41], gives little additional information on the structure of the molecule. The relatively small gradient for the methyl protons suggest that this group is trans to the carbonyl. Since the ring is non-planar, the principal axis of complexation is difficult to define without detailed knowledge of the geometry.

It does appear, however, that the europium atom is closer to the adjacent methylene group than to the exocyclic double bond. A number of conformations may be similar in energy but it appears that interconversion of enantiomers may only be brought about by rotation of the carbonyl group through the ring, since any arrangement with all thirteen atoms coplanar is severely strained.

It is interesting that with increasing concentration of shift reagent, the increase in shift of the olefinic protons H_d,H_e,H_i and H_j is large compared to the other protons, again suggesting a number of accessible conformations.

Thus the spectral data provides overwhelming evidence that the purified product is not 2-vinylcycloundeca-5,9-dien-1-one, [10], but the tautomeric form, 2-(methylethylene)cycloundeca-5,9-dien-1-one, [38]. It is also clear from the I.R. spectrum of the unpurified product that the rearrangement takes place on the alumina column. In addition, none of the original product [10], was recovered, indicating that an extremely specific and facile conversion is taking place, which suggests that interaction of [10] with the alumina surface is promoting the prototropic shift to produce [38] in preference to [10]. In a favourable case even neutral alumina might be expected to promote the keto-enol equilibrium necessary to initiate rearrangement. The fact that only one of two possible stereoisomeric products is formed suggests

a steric preference for the transoid enol in the absorbed state and reprotonation must occur exclusively on this conformer if the isomerisation is kinetically controlled.

2.4 Other Reactions

In the reaction of the intermediate [8] with dichloroacetone [25] (see 2.2), it appears that the carbonyl carbon atom of [25] reacts with the π-allyl groups of [8] in preference to the terminal, chlorine bearing, carbon atoms. It was considered that this may in part be due to the electron-withdrawing effect of the oxygen atom making the carbonyl carbon atoms particularly susceptible to nucleophilic attack by [8]. It was therefore decided to repeat the experiment using similar three carbon compounds with a less reactive central carbon atom and/or more reactive terminal carbon atoms. The compounds chosen were 1,1-bis(chloromethyl)ethylene [17], 1,1-bis(iodomethyl)ethylene [26] and malonyl dichloride [27].

[17] was prepared by chlorination of methallyl chloride in carbon tetrachloride. After purification by spinning band distillation, (b.p.=74°C @ 140mmH_g), an excess of the dichloro compound was added to a solution of [8] in benzene.

A G.L.C./M.S. of the products revealed the presence of three compounds of molecular weights 162, 218 and 216, the molecular weights being given in the order in which the compounds were eluted from the G.L.C. column. The major fraction was that with the molecular weight of 218. However, none of the mass spectra showed a strong parent peak, suggesting that the products are acyclic, nor do the fragmentation patterns fit the desired structure. The compounds do however appear to be pure hydrocarbons, as the mass spectra show no n/n+2 doublets in the ratio of 3:1 characteristic of chlorine. Mass spectrometry does not distinguish of course, between the isomeric (CH_2=C(CH_2)) and (CH_2CH=CH CH_2-) units possible in the product.

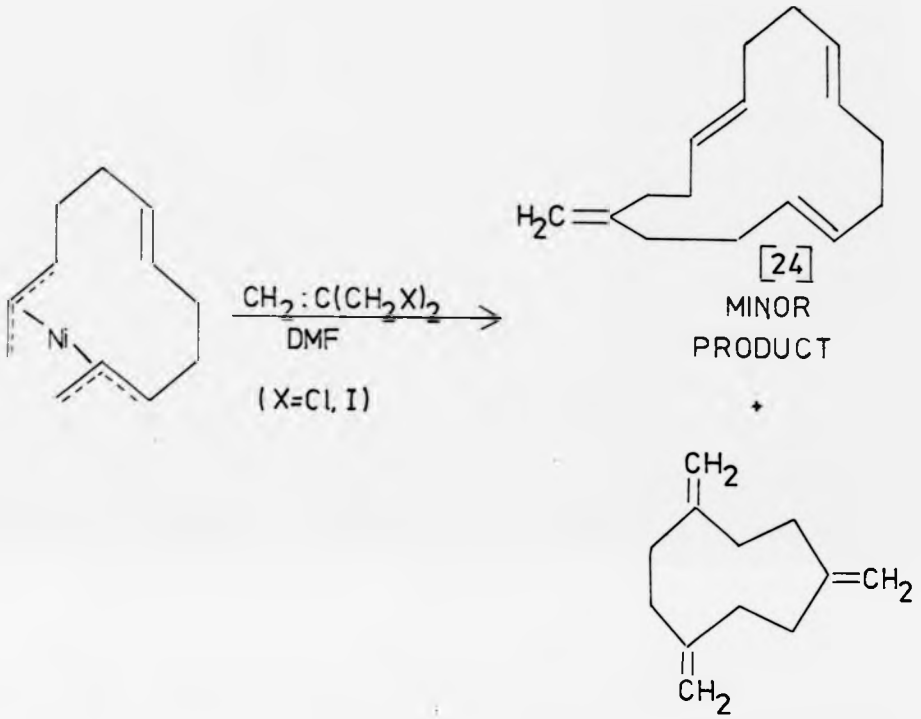
To attempt to make the reaction more facile, a mildly nucleophilic solvent, dimethylformamide (D.M.F.), was used to allow the nickel to be more easily detacted in the course of the reaction. (A control reaction was first carried out to ensure that D.M.F. was not a sufficiently strong Lewis base to cause ring closure of the π-allyl complex. A solution of [8] in D.M.F. showed no charge in its N.M.R. spectrum even after 18 hours).

An N.M.R. spectrum of a solution containing a mixture of products from this reaction, showed the appearance of a peak at 5.2τ which may have been due to the presence of 1,4,7-trimethylenecyclononane, [16], formed by catalylic trimerisation of [17], as reported by Corey[5]. This compound has two resonances, 5.2τ and 7.7τ, the latter resonance, in our spectrum, would be hidden by proton resonances of the other products.

If this reaction was occurring then it is reasonable to assume that it would occur equally well with bis-cyclooctadiene nickel. To test this a control reaction was carried out, adding a solution of [17] in D.M.F. to a solution of bis(cyclooctadiene) nickel in benzene. The N.M.R. spectrum of the products of this reaction clearly showed two resonances one at 5.2τ and the other at 7.7τ, with integrals in the correct ratio (1:2) for the trimeric compound [16], and this, together with the infra-red spectrum which showed the strong absorption at 6.07μ, quoted by Corey[5], suggests that [16] was indeed present.

The N.M.R. spectrum of the reaction between [8] and bis(iodomethylethylene [26] in D.M.F. showed that a considerable proportion of the product is the trimer, 1,4,7-trimethylenecyclononane
7.7τ in the ratio of 1:2. Absorptions at 6.07 and 11.15μ in the I.R. spectrum, characteristic of $>C=CH_2$, support this conclusion.

A mass spectrum of the products provided some evidence that a


Ni
CH2 : C(CH2X)2
DMF
(X=Cl, I)
H2C
[24]
MINOR
PRODUCT
CH2
=CH2
CH2
[16]
MAJOR
PRODUCT

[SCHEME 4]

small amount of the desired 1:1 addition product [24] had been formed. There was a molecular ion of 216, which is the correct molecular weight of [24], and also, the fragmentation pattern, - loss of $-CH_3$ followed by stepwise elimination of $-CH_2$, is as expected for the product.

The sample also appeared to contain another compound, (molecular ion 162), which may have been 1,4,7-trimethylenecyclononane, cyclododecatriene or both. This was supported by the N.M.R. spectrum of the chromatographed product, which showed that the products were not separated by chromatography and indicated the presence of three substances:

a) Cyclododecatriene - resonances at 5.0 and 7.97τ [7]

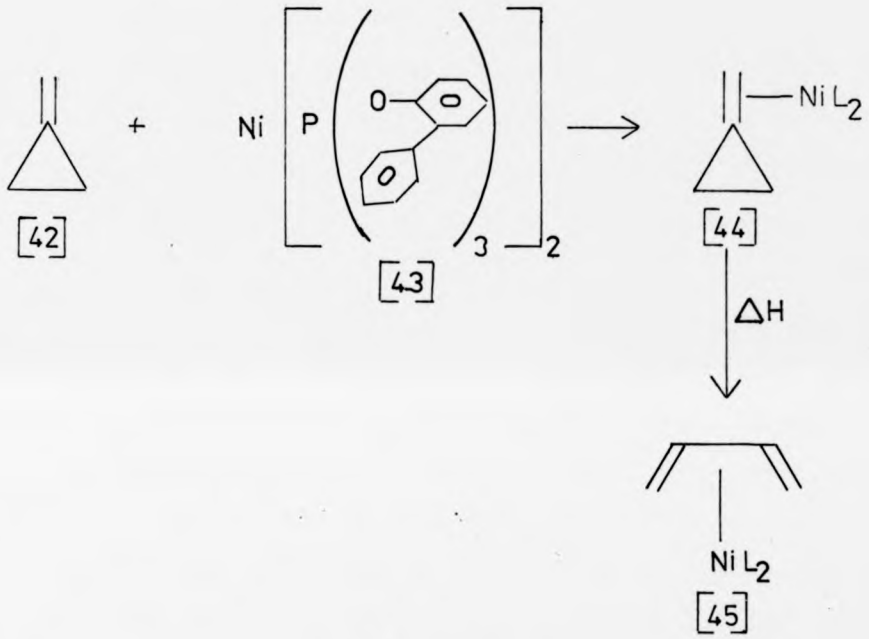
b) 1,4,7-trimethylenecyclononane - resonances at 5.2 and 7.7τ

c) A third compound with resonances at 4.60, 4.92, 8.00 and 8.35τ

Although the impurity of the sample made reasonable integration difficult, the peaks in (C) appeared to be in the correct ratio expected for methylenecyclopentadeca-4,8,12-triene [24], i.e. 6:2:12:4 respectively, and this, in conjunction with the mass spectrum, provides reasonable evidence for the presence of a small amount of this compound. However, the addition reaction appears to be in competition with the cyclotrimerisation reaction, (see Scheme [4]), and since the products are difficult to isolate, it does not provide a suitable route for preparation of reasonable quantities of [24].

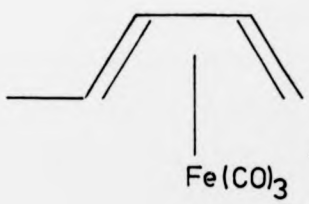
The only product of the reaction of the intermediate [8] with malonyl chloride, $CH_2(COCl)_2$, was a brown polymeric solid which did not soften below 360°C.

Combustion analysis of the brown polymer gave C-73.41%; H-7.26%; O-16.39% and Cl-1.16% suggesting that the product may be essentially a polymer of formula $HOOCCH_2CO(C_{12}H_{16}-COCH_2CO)_nOH$.

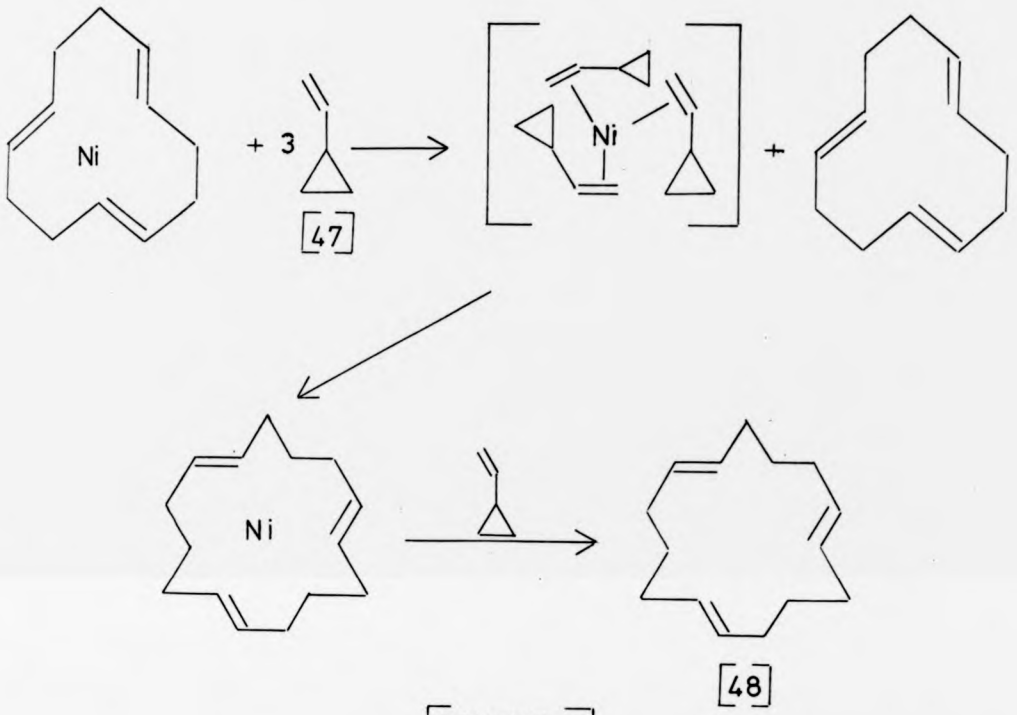


[42] [43] [44] [45]

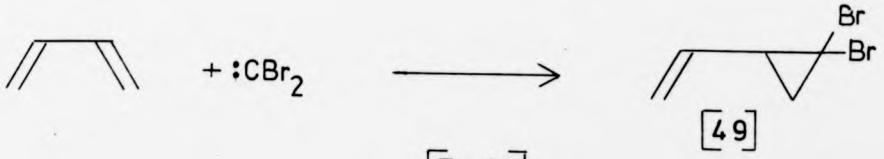
[Eq 21]



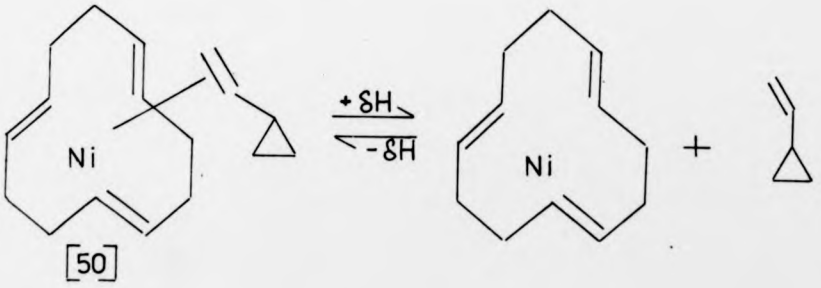
[46]



[SCHEME 5]



[Eq 22]



[SCHEME 6]

2.5 Reaction with Vinylcyclopropane

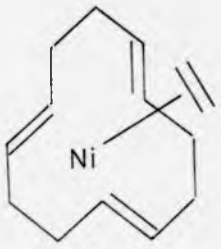
It has been reported[8] that methylene cyclopropane, [42], will react with NiL_2, where L=tri(o-phenylphenyl)phosphite, [43], to produce the stable 1:1 addition compound [44], which on heating undergoes ring fission to produce [45], (see Eq.21). Similar ring opening, of vinyl cyclopropane, occurs on complexation with the iron tricarbonyl group to produce [46][9].

Since it appears that $CH_2{:}C(CH_2X)_2$, (X=Cl,I) [17], [26], will cause ring closure of [8], displacement of the cyclododecatriene formed and subsequent trimerisation to produce 1,4,7-trimethylene-cyclononane [16], it was considered that a similar reaction, involving ring opening might also occur with vinylcyclopropane, [47], to produce the fifteen membered carbocyclic ring [48], (see Scheme 5).

The vinylcyclopropane was prepared by debromination of 2,2-dibromo-1-vinylcyclopropane [49] which in turn was prepared by reaction of dibromocarbene with butadiene, (see Eq.22).

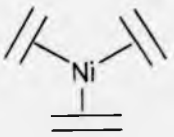
[47] did not react with $[COD]_2Ni$, [5], at room temperature, even after 60 hours, while at higher temperatures, decomposition occurred to produce cyclooctadiene, vinylcyclopropane and metallic nickel. Reaction of [47] with cyclododecatrienenickel [7], at $-10^{o}C$, resulted in the formation of a yellow compound in solution which, on warming slightly, reverted to red. The yellow compound was reformed on cooling the solution back to $-10^{o}C$. Warming the reaction to room temperature resulted in decomposition to produce cyclododecatriene, vinylcyclopropane and metallic nickel.

Thus, the displacement reaction does occur at room temperature, with cyclododecatriene being displaced more easily than cyclooctadiene, but it appears that the vinylcyclopropane/nickel complex, if it is formed at all, is unstable and immediately decomposes to metallic nickel and vinylcyclopropane. The colour range in the reactions with [7] is ascribed to a reversible thermal, coordination/dissociation reaction occurring between [7] and a molecule of vinylcyclopropane, (see Scheme 6).

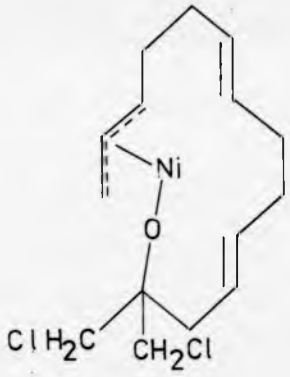


[a]

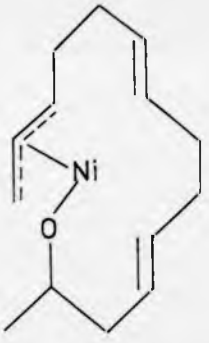
[51]



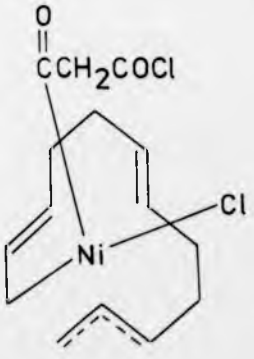
[b]



[52]



[53]



[54]

Subsequent to this work, the Max Plank group[13] has shown that a number of simple olefins, including ethylene, displace trans, trans, trans cyclododecatriene from the complex [8]. Initially, the species [51a] is presumably formed and this is then c onverted into the tris-ethylene complex [51b] which is isolable and stable under an atmosphere of ethylene. It is possible that the vinylcyclopropane analogue is formed in our system, although it proved non-isolable.

2.6 Discussion

While Wilke and co-workers have clearly demonstrated that the dodeca-trienyl complex [8] will undergo insertion reactions with carbon monoxide[1] and alkyl isocyanides[10], similar insertion reactions do not appear to occur readily with larger groups.

It was hoped that in the reaction of [8] with dichloroacetone, the terminal, chlorine bearing carbon atoms would add simultaneously to the two π-allyl groups of [8], to produce cyclopentadecatrienone [34]. This clearly does not occur, the major product of the reaction being instead the linear tetrachloro compound [35]. Thus it appears that the initial step in the reaction is the formation of an intermediate such as [52], since it has been shown[11] that a similar intermediate [53], is formed in the reaction between [8] and acetaldehyde. In the latter case, the remaining π-allyl group in [53] does not have the same reactivity towards acetaldehyde as the first and will only react with a second molecule in the presence of a strongly co-ordinating ligand, (e.g. cyanide ion or carbon monoxide) which, by co-ordination to the nickel atom, causes the formation of a σ-allyl so enhancing the reactivity towards the electrophilic carbonyl carbon atom of acetalde-hyde. It is not clear whether this also applies in the reaction of [52] with a second molecule of dichloroacetone since the reaction mixture was not studied in order to determine whether the product or the inter-

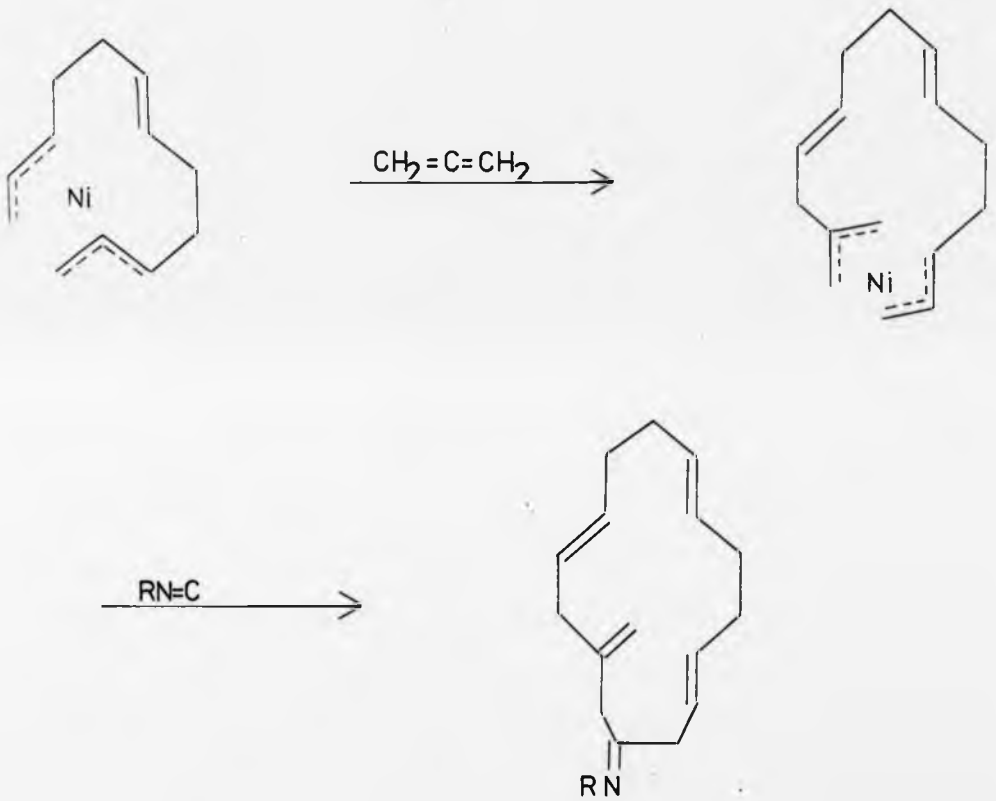
mediate were present, prior to the addition of diethylene triamine. It may be that the electron-withdrawing effect of the chlorine atoms make the carbonyl carbon atom sufficiently electrophilic to react with the second π-allyl group. On the other hand, addition of diethylene triamine may allow the reaction to proceed in the manner described for acetaldehyde.

Formation of linear rather than cyclic products, due to preferential attack at the carbonyl carbon atom forming the intermediate [52], prompted the reaction of [8] with malonyl chloride in the hope that the two terminal carbonyl groups would react with the two π-allyl groups to produce a cyclic fifteen carbon compound. However, it appears that in this reaction the intermediate is probably [54], as a similar intermediate is reported for the reaction between [8] and acetyl chloride[11]. Once [54] is formed, the free end of the malonyl chloride may be unable to react with the second π-allyl group due to steric factors and/or the decreased reactivity of the allyl[11]. Instead, it would react with another molecule of [8] or [54], resulting in the production of the brown polymeric compound which was obtained.

Reaction of [8] with $CH_2:C(CH_2X)$, (X=Cl I), particularly in the presence of dimethylformamide, results in the formation of considerable quantities of 1,4,7-trimethylenecyclononane [16]. Since the products contain cyclododecatriene, the reaction presumably proceeds by ring closure of the bis π-allyl, followed by displacement of cyclododecatriene and cyclotrimerisation of $CH_2:C(CH_2X)_2$. The iodo compound [26] in DMF did produce a small amount of the desired product [24]. It may be that in this case the increased reactivity of the iodine together with the co-ordinating effect of the DMF enhanced the reactivity of the second π-allyl group in the intermediate sufficiently to allow the cyclisation to occur. The fact that displacement of the π-allyl by $CH_2:C(CH_2I)_2$ was probably occurring may also have been important in altering the three

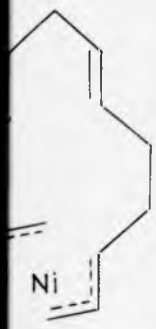
dimensional structure and so bringing the two ends of the molecule into a suitable position for reaction to occur. However, it is clear that since only a small amount of [24] is produced, the main reaction is displacement of the bisπ-allyl followed by cyclotrimerisation of [26] to form [16]. It was this that led to the attempted cyclotrimerisation of vinylcyclopropane by displacement of either cyclooctadiene from bis-(cyclooctadiene) nickel [5], or cyclododecatriene from cyclododecatriene nickel [7]. The failure of this experiment was presumably due to the inability of vinylcyclopropane to form a stable complex with the nickel subsequent to displacement of the original ligand.

The main purpose of this work was to attempt to find, from inexpensive bis π-allyl nickel complexes, a synthetic route to fifteen-membered carbocyclic rings which could be readily converted into musk-type compounds. Success in this was limited to the production of a small amount of [24] in the reaction between [8] and [26], but this is not a suitable method for large scale production. The lack of success of the chosen approach to this problem is due, to a large extent, to the formation of intermediates of the type described by Baker[11] resulting in the deactivation of the second π-allyl group, to the free end of the reactant. Unfortunately, this effect was not reported in time for it to be taken into consideration in this work. However, Baker and co-workers[12] have avoided this problem by reacting the intermediate complex [8] with allene to produce the new bis π-allyl complex [28], (see Eq.18), which, after reaction with carbon monoxide at 0-10^{o}C, produces the fifteen-membered cyclic ketone [29], which on hydrogenation, produces muscone. However, in this case also, the yield is small being only 4-5% of the total product. The problem of low yield was subsequently solved by carrying out the second insertion reaction with ethyl



SCHEME 7

isocyanide rather than carbon monoxide, permitting a short, efficient synthesis of racemic muscone from butadiene and allene[14], (Scheme 7).



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CHAPTER 3

EXPERIMENTAL

3.1 Techniques Used In Handling Air-sensitive Compounds

The three essential pieces of apparatus required for manipulating air sensitive compounds were

1) a vacuum line used in conjunction with a nitrogen line, Fig.[30]
2) Schlenk tubes, [31]
3) Submerged, positive pressure filtration tubes, [31]

The technique for filtration is illustrated in Fig.[31]. One end of the flexible filtration tube is passed through a tight-fitting hole in a suba-seal. A piece of filter paper is put over the end of the tube and held in place with nichrome wire. A positive pressure of nitrogen is maintained in the schlenk tube A so that when the stopper is removed in order to insert the filtration tube, there is a constant outflow of nitrogen so preventing oxygen entering the schlenk tube. After the filtration tube is inserted the schlenk is sealed with the suba-seal. At this stage, the filtration tube is not immersed in the solution to be filtered but is suspended above it, allowing nitrogen to blow through the tube to remove any oxygen therein. The other end of the filtration tube is then passed through a second suba-seal and inserted into schlenk tube B in the manner previously described. B is then quickly connected to the atmosphere via a mercury one-way valve. This allows a stream of nitrogen to pass from schlenk A, through the filtration tube into schlenk B and hence into the atmosphere. Filtration is achieved merely by submerging the filtration tube in the solution in A. This allows a positive pressure of nitrogen to build up in A which forces the liquid through the filter paper and into B, leaving any insoluble material in A. If the filtration is slow, then the pressure which builds up in A has to be released periodically using a by-pass in the nitrogen line.

The technique can also be used to transfer liquids, e.g. solvents. This is particularly useful where the solvents need to be kept at a low temperature, as the transfer is rapid and in addition the filtration tube can be lagged along its length with cotton wool soaked in a liquid at suitable temperature.

In all the experiments performed, further care was taken to prevent oxidation by thoroughly degassing all solvents prior to use and working in an inert atmosphere of pure, dry nitrogen.

3.2 Preparation of Pure, Anhydrous, Nickel (II) Acetylacetonate

Commercial nickel acetylacetonate invariably contains some water of crystallisation, therefore it was necessary to make the salt completely anhydrous prior to use.

A solution of nickel acetylacetonate (200g) in toluene (800ml) was refluxed using a Dufton column and the water removed by azeotropic distillation. When there was no longer any water in the distillate, the distillation was halted and the remainder of the solution was reduced in volume on a Buchi Rotavap and the dark green crystals of nickel acetylacetonate were allowed to crystallise from the toluene. These were then recrystallised a second time from toluene. The crystallisation was very slow (1-2 days) but does yield large crystals of pure anhydrous nickel acetylacetonate. The product was filtered under dry nitrogen, to prevent the entry of water vapour, and then dried by removing residual solvent under high vacuum.

3.3 Synthesis of bis(cyclooctadiene) Nickel (o)[1]

Nickel acetylacetonate (3.85g) was dissolved, under nitrogen, in redistilled, dry benzene (38.5ml) and redistilled 1,5-cyclooctadiene (3.85g) was added. After cooling to $0^{o}C$, diethylaluminium ethoxide (4.49g) was added dropwise with stirring over 1½ hours. After 15 hours at the same temperature, yellow crystals of bis(cyclooctadiene) nickel were obtained. The crystals

were filtered and washed three times with fresh benzene. The mother liquor, on standing for 24 hours, produced a second crop of crystals which were also filtered and washed. The total yield of product was 3.95g (88%). An N.M.R. spectrum in perdeuterobenzene gave two peaks at 5.54τ and 7.79τ in the ratio of 1:2.

3.4 Synthesis of t,t,t-cyclododecatriene nickel[1]

Anhydrous nickel acetylacetonate (14.8g) and redistilled t,t,t-1,5,9-cyclododecatriene (20g) were dissolved in degassed diethyl ether (193ml). The mixture was cooled to 0°C and diethylaluminium ethoxide (15.7g), in degassed diethyl ether (20ml), was added dropwise, with stirring over 2 hours. The reaction mixture was left to stir for a further 48 hours at 0°C. The solution was concentrated and cooled to -78°C, when crystals were formed. These crystals were a mixture of aluminium acetylacetonate and cyclododecatriene nickel. The mother liquor was filtered off, the cyclododecatriene nickel was taken up in isopentane, filtered and recrystallised from the solution. The supernatent was again removed and the crystals were once again recrystallised from isopentane to give deep red cyclododecatriene nickel (0), which was dried under high vacuum. Yield = 9.6g (76%) N.M.R. spectrum gave resonances at 5.7τ and 7.95τ in the ratio of 1:2.

3.5 Synthesis of Dodeca-2,6,10-triene-1,12-diyl Nickel [8], From Bis (Cyclooctadiene) Nickel and Butadiene

Bis(cyclooctadiene) nickel (8g) was reacted for 7 hours at -40°C with 50ml butadiene under nitrogen. The solution was then filtered at -40°C and the butadiene removed by vacuum at -40°C. Cyclooctadiene was removed under high vacuum between -20° and +20°C. The residue was dissolved in a minimum amount of isopentane and crystallised at -78°C. The supernatent liquid was removed and recrystallisation from pentane produced red/brown crystals, (2.6g, 43% yield), m.p. 0-1°C. N.M.R. spectrum: H_e-4.8τ, H_b-5.8τ; H_c-5.99τ; H_a-6.88τ and H_d- a broad band

centred at 8.05τ. The crystals were air sensitive but could be stored for several months at -40°C under nitrogen.

3.6 Synthesis of Dodeca-2,6,10-triene-1,12-diyl nickel [8] from Cyclododecatriene nickel (0) and butadiene

Butadiene (50ml) was distilled onto cyclododecatriene nickel (0) at -40°C. The mixture was stirred for 3 hours at that temperature, filtered and the excess butadiene removed, with the temperature still at -40°C. Free cyclododecatriene was then removed under high vacuum between -20 and +20°C. The residue was dissolved in the minimum amount of pentane and crystallised at -78°C. It was then recrystallised from pentane to give red/brown crystals (2.9g; yield 36%) which melted between 0-1°C. The N.M.R. spectrum was identical to that of the previous experiment.

3.7.1 Reaction of the Intermediate Complex [8] with Dichloroacetone

The bis π-allyl complex [8], (1.2g), was dissolved in benzene and to this was added dichloroacetone (excess), dissolved in benzene, at 0°C. The mixture was stirred for 2 hours after which time, diethylene triamine was added to remove the nickel. A deep red precipitate of nickel salts was formed leaving a clear, red/brown benzene solution. This was filtered and concentrated on a Büchi Rotavap and passed through a neutral alumina column, eluting with a 1:1 mixture of diethyl ether and chloroform. The solvent was removed by vacuum evaporation, to leave an orange-yellow oil with a characteristic odour (0.8ml). N.M.R. and I.R. spectra were taken, (see Table 1).

3.7.2 Hydrogenation of the Product of the Reaction between [8] and Dichloroacetone

A portion of the reaction product (80mg) was dissolved in methanol (1.5ml) and hydrogenated over platinum black, using a 5ml capacity microhydrogenator. 64ml, (5.7mg) of hydrogen was absorbed. Removal of solvent, in vacuo,

gave a white waxy solid. C,67.5; H, 9.1%. N.M.R. and I.R. spectra were taken. (see Table 2).

3.7.3. Reduction of the Hydrogenated Product Using Lithium and Liquid Ammonia

Liquid ammonia (50ml) was dried by stirring with metallic sodium at $-35^{o}C$. It was then distilled into a 250ml, 3-necked flask, equipped with a magnetic stirrer and a dry ice/acetone condenser. Lithium was then added, (50mg), in small pieces, and the solution stirred at $-80^{o}C$, until all the lithium dissolved. Diethyl ether, (10ml), precooled to $-20^{o}C$, was then added dropwise over 5 minutes. The bath at $-80^{o}C$ was then replaced by an ice/salt bath at $-18^{o}C$. The temperature of the dry ice condenser was allowed to rise to $-20^{o}C$. The solution was then stirred under a stream of nitrogen for 1 hour until most of the ammonia was removed and golden brown globules were formed, floating on the surface of a clear solution. The hydrogenated product, (42mg) dissolved in 10ml of diethyl ether at $-20^{o}C$, was then slowly added. After addition was complete the solution was stirred for a further 30 minutes. Wet diethyl ether, (50ml), was then added, followed by 50ml of water. The mixture was separated in a separating funnel, the ether layer being washed with two 25ml portions of water and dried over anhydrous potassium carbonate. The ether was removed by suction and left a colourless oil which was distilled by microdistillation. Total product = 25mg. An N.M.R. spectrum indicated that the only significant resonance was a broad singlet at 8.75τ.

3.8.1 Preparation of 3-chloro-2-chloromethylpropene by Chlorination of 2-chloromethylpropene (methallylchloride)

Methallyl chloride (250ml) was added to 500ml of carbon tetrachloride in a 5-necked flask and a chlorine/air mixture was slowly bubbled in, with stirring at $-30^{o}C$. Air was also blown through the reaction flask

to effect a more rapid removal of hydrogen chloride. The reaction was stopped when excess chlorine was detected in the effluent gas stream. The reaction mixture was then washed several times with water to remove hydrogen chloride and allowed to stand overnight over anhydrous potassium carbonate to dry and to neutralise any acid. The carbon tetrachloride was then removed on a Büchi rotavap and the residue distilled on a spinning band distillation unit.

There was obtained successfully ;-

i) 2-chloromethyl 1-chloropropene. Bp 67°C @ 140 mmHg;

ii) 2-chloromethyl-3-chloropropene. Bp 74°C @ 140 mmHg;

iii) 2-methyl-1,2,3-trichloropropane. Bp 99°C @ 140 mmHg.

The desired product (ii) was obtained in 30% yield and identified by its N.M.R. spectrum and refractive index.

N.M.R. - 2 singlets at 5.81 and 4.68τ in ratio of 2:1

R.I. $n^{25}D$ = 1.4728

3.8.2 Reaction of the Intermediate Bis π-allyl Complex [8] with 2 Chloromethyl-3-chloropropene

The intermediate complex [8] (3.3g) was dissolved in 20ml benzene and cooled to -5°C. The solution was then stirred while the dichloride, (2.8g) in 10ml benzene was added dropwise over two hours. The solution was stirred for a further 3 hours at -5°C and then allowed to come to room temperature overnight, producing a dark red solution. This was syringed into 500ml water to give a green aqueous layer and a white opalescent benzene layer. The benzene layer was seperated, washed with water, dried over anhydrous potassium carbonate and the benzene removed, leaving a deep yellow oil. The olefinic compounds in the oil were then isolated by preparative thin layer chromatography on silica gel, using benzene as solvent. A second preparative thin layer chromatogram of the olefinic compounds using cyclohexane as solvent gave three bands, which, on gas/liquid chromatography on a 6 foot E301 column at 140°C, revealed

that all three fractions contained cyclododecatriene together with a second product represented by a broad absorption with a longer retention time than cyclododecatriene. This fraction was collected as it was eluted from the column using glass baffle tubes cooled in dry ice. G.L.C./M.S. analysis revealed three compounds of molecular ion 162, 218 and 216.

3.8.3 Reaction Between the Intermediate Complex [8] and 2-chloromethyl-3-chloropropene in Dimethyl Formamide (D.M.F.)

The intermediate complex (0.5g) was dissolved in 10ml benzene. The solution was then cooled to -10°C while 2-chloromethyl-3-chloropropene (0.3g) in 10ml dry D.M.F. was added slowly with stirring. The mixture was then stirred for 2 hours at -10°C and allowed to come to room temperature overnight. A black precipitate of nickel and a pale blue solution resulted. The solution was filtered, washed with water, extracted with benzene and dried over anhydrous potassium carbonate. The benzene and D.M.F. were then removed under vacuum. N.M.R. spectrum of the impure product in CCl_4 gave resonances at 4.47τ; 4.95τ; 7.1τ(D.M.F. doublet); 7.6τ and broad peak centred at 7.92τ.

3.8.4 Reaction between Bis(cyclooctadiene) Nickel [5], and 2-chloromethyl-3-chloropropene, [17], in Dimethyl Formamide

To bis(cyclooctadiene) nickel, (0.6g) was added, at 0°C, a solution of [17] in 20 ml of a 1:1 mixture of benzene:D.M.F. The mixture was stirred, allowed to come to room temperature and reacted overnight to produce a blue solution. The product was extracted as in the previous experiment. N.M.R. spectrum: 4.85, 5.0, 5.2, 5.8, 5.98, 7.1(D.M.F. doublet), 7.6, 7.7 and 7.85τ. The resonances at 5.2 and 7.7 are strong and in the ratio of 1:2.

3.9.1 Preparation[2] of 2-iodomethyl-3-iodopropene [26]

2-chloromethyl -3-chloropropene (60g, 0.48 mole), was added to potassium iodide (160g, 0.96 mole), in 1 dm^3 acetone. A precipitate formed immediately. The mixture was refluxed for eight hours, filtered and concentrated to 250ml by distillation. The concentrate was poured into 800ml water and extracted with 250ml pentane. The pentane solution was washed with sodium thiosulphite solution and water and dried over anhydrous sodium sulphate. The pentane was removed by distillation and the product was distilled through a Vigreux column, (b.p. 85°C at 5mm Hg). The product, which crystallised on cooling, was washed with sodium thiosulphite and recrystalliesed from hexane to give white plates. m.p. 32-33°C, (105g, 71%).

3.9.2 Reaction between the Intermediate Complex [8] and Diiodoisobutene ($CH_2:C(CH_2I)_2$) [26]

The intermediate complex [8] (0.2g) was dissolved in D.M.F. (5ml) and to this was added a solution of diiodoisobutene (0.3g) in D.M.F. (5ml). The reaction mixture was stirred at -10°C for 5 hours giving a yellow solution. It was then allowed to come to room temperature and react for a further 48 hours, at the end of which time the solution had turned green. The reaction mixture was partitioned with pentane and water, the pentane fraction dried over anhydrous potassium carbonate and chromatographed on a neutral alumina column using pentane as elutant. The solvent was then removed leaving a mixture of products including cyclododecatriene, ^{1}H N.M.R. resonances at 5.0 and 7.97τ, M(mass spectroscopy), 162; 1,4,7-trimethylenecyclononane [16], I.R. absorptions at 6.07 and 11.15μ, ^{1}H N.M.R. resonances 5.2 and 7.7τ, M 162; and a third compound with ^{1}H. N.M.R. resonances 4.60, 4.92, 8.0 and 8.35τ in the ratio of 6:2:12:4 and M 216.

3.10 Reaction of the Intermediate Complex [8] with Malonyl Chloride $CH_2(COCL)_2$ [27]

The intermediate complex [8] (6.75g) was dissolved in 150 ml of dried degassed diethyl ether and stirred at -78°C, under nitrogen. Malonyl chloride (4.28g) was dissolved in 150ml diethyl ether and added dropwise. The reaction was allowed to come to room temperature overnight. It was then filtered to give a red etheral solution, leaving a brown solid. The ether was removed, followed by cyclododecatriene under high vacuum to leave a fairly mobile red/brown oil which gave a featureless N.M.R. spectrum, suggesting it to be polymeric. The brown solid residue was treated with dilute hydrochloric acid to remove traces of metallic nickel, then neutralised with potassium carbonate solution and washed with diethyl ether. Soxhlet extraction was then carried out, with water, to remove nickel chloride leaving a brown polymeric solid which was insoluble in all solvents tried.

Mpt $>$ 360°C.

Elemental analysis - C-73.41%; H-7.26%; O-16.39%; Cl-1.16%

On heating under high vacuum at 400°C the product decomposed to give a black residue and an orange oil.

3.11 Synthesis of Vinylcyclopropane

3.11.1 Preparation of Potassium Tertiary Butoxide/tertiary Butanol

Potassium metal (40g) was dissolved in anhydrous t-butyl alcohol (450ml) and the excess alcohol removed by distillation. As the alcohol was being removed, n-heptane (400ml) was added slowly through a dropping funnel. The n-heptane was then also removed. (The purpose of the n-heptane was to allow the potassium tertiary butoxide to precipitate as a powder rather than forming a solid cake). The flask was then heated to 90°C and pumped down to a pressure of 0.6mm Hg, to obtain the dry product (160g)

which was a 1:1 molar ratio of potassium tertiary butoxide/tertiary butanol. This mixture is much more effective for carbene reactions than the pure potassium tertiary butoxide.

3.11.2 Preparation of 1,1,dibromo-2-vinylcyclopropane[3] [49]

A 1:1 mixture of potassium tertiary butoxide/tertiary butanol (90g) was placed in a 2 litre flask, fitted with a mechanical stirrer, thermometer, dropping funnel and nitrogen bubbler. The flask was then cooled in a carbon tetrachloride/dry ice bath. A slurry was made of the potassium tertiary butoxide by distilling in 1,3butadiene (150g) and to this was added bromoform (125g - redistilled) in pentane (200ml) at such a rate that the temperature never exceeded $-10^{o}C$. After the addition was complete, the reactants were stirred for an additional hour and then diluted with pentane and water. The organic layer was separated, washed with cold water, dried overnight over anhydrous sodium sulphate, the solvent removed on a Büchi rotavap and the residue distilled through a Vigreux column. An initial forerun of bromoform was obtained, followed by a fraction boiling at $69.5^{o}C$ at 25mm Hg which was found by N.M.R. to be 1,1,dibromovinylcyclopropane (90g - 80% yield).

3.11.3 Debromination of 1,1,dibromovinylcyclopropane to form vinylcyclopropane

1,1,dibromovinylcyclopropane (70g) and dioxane (165ml) were placed in a 2 litre, 5-necked flask, equipped with a mechanical stirrer, pressure equalised dropping funnel, and an air condenser, the top of which was fitted with a thermometer, and led to a dry ice/acetone condenser via a spiral condenser. The remaining two necks of the flask were stoppered and the flask cooled with running water. A mixture of ethanol (820ml) and water (30ml) was then added dropwise and at the same time, small pieces of sodium (total 115g) were added intermittently, via one of the stoppered

necks. After all the sodium had been added and the reaction ceased, water (500ml) was added and the flask heated in a water bath to 60^{o}-70^{o}C for one hour. The reaction product, which was collected in the dry ice trap, was dried by metallic sodium and redistilled through a Dufton column. The product, b.pt. 40^{o}C, was identified by N.M.R. as vinylcyclopropane. (13.2g - 62%)

3.11.4 Reaction of Vinylcyclopropane with Bis(cyclooctadiene) nickel (0)

Vinylcyclopropane (2g) was distilled onto bis(cyclooctadiene) nickel (0) (1.6g) in a schlenk tube and the mixture stirred at room temperature for 60 hours. At the end of this time, N.M.R. spectrum showed that no reaction had occured. The mixture was then heated to 50^{o}C overnight when it was found to have decomposed leaving vinylcyclopropane, cyclooctadiene and metallic nickel.

3.11.5 Reaction of Vinylcyclopropane with Cyclododecatriene Nickel

Vinylcyclopropane (1.5ml) was distilled onto cyclododecatriene nickel (0.4g) in a schlenk tube and allowed to react at -10^{o}C for 24 hours. A yellow compound was formed in solution which on warming slightly reverted to the original red colour. The reaction was then allowed to come to room temperature, resulting in precipitation of metallic nickel. The volatile componant was then distilled off and found to be pure vinylcyclopropane. The residue was washed with pentane, centrifuged to remove metallic nickel, and G.L.C. and N.M.R. spectra taken, showing that only cyclododecatriene was present, ^{1}H N.M.R. resonances at 5.0 and 7.97τ.

3.12 Reaction of the Intermediate bis-π-allyl complex [8] with carbon monoxide[4]

The intermediate complex [8] (11.3g) was dissolved in 150ml pentane in a large schlenk tube, and cooled to -78^{o}C and stirred. Carbon monoxide was

then bubbled in and the mixture allowed to react for 24 hours until no more carbon monoxide was absorbed. The pentane and nickel tetracarbonyl thus formed were then removed in vacuo, the nickel tetracarbonyl being destroyed by a bromine trap. An infra-red spectrum of the residue showed it to be 2-vinylcycloundeca-5,9-dien-1-one, (carbonyl absorption at 1712cm^{-1}), together with some cyclododecatriene. The product was then purified by chromatography on a neutral alumina column eluting with pentane. Infra-red and N.M.R. spectra (Figs. [39] and [40]) showed that the eluate was distinctly different from the crude product.

The N.M.R. spectrum of the purified product was then analysed further by lanthanide-induced shift experiments. The product, (30.1mg, 1.58mM), was dissolved in carbontetrachloride in an N.M.R. tube and a spectrum taken. Eu(fod)$_3$, (28.1mg, 0.203mM), was then added to the solution and the spectrum rerun. More Eu(fod)$_3$, (35.8mg - total 63.9mg, 0.462 mM) was added and a third spectrum taken.

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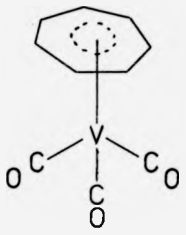
PART TWO



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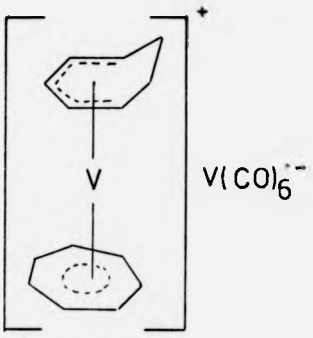

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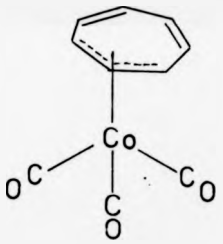


[3]

CHAPTER 1

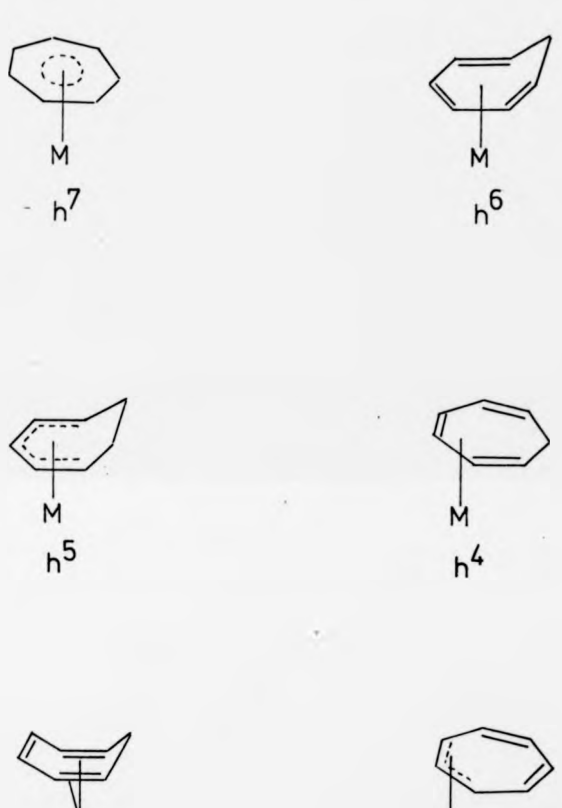
A considerable number of transition metal complexes with 1,3,5 cycloheptatriene or tropylium have been prepared and characterised, together with some of their reactions, a number of the latter having been described earlier in this thesis.

Thus titanium or zirconium chloride (MCl_4) reacts with cycloheptatriene to give the complex $[MCl_2(C_7H_7)_2]$[1] while in group V the only reported complexes are $C_7H_7V(CO)_3$ and $[C_7H_7VC_7H_8][V(CO)_6]$, [1] and [2], prepared by reaction of C_7H_8 and $V(CO)_6$[2].

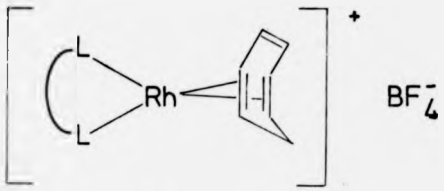
The only complex formed with group VII is the mixed sandwich cation $[C_7H_7RMnC_5H_5]^+$. Of the group VIII metals cobalt, rhodium and iridium, the only cycloheptatrienyl complex reported is $C_7H_7Co(CO)_3$, prepared by the photochemical reaction of $Co_8(CO)_8$ with cycloheptatriene[3]. In this compound, variable temperature ^1H N.M.R. studies[4] have shown that the cycloheptatrienyl ring has h^3 co-ordination to the metal and that the molecule is fluxional [3].

There are reports in the literature of complexes produced as a result of reaction between rhodium and iridium compounds and cycloheptatriene Bonati and Wilkinson[5] state that the reaction between rhodium dicarbonylacetylacetonate, $Rh(CO)_2(acac)$, and cycloheptatriene produces in low yield, the bicyclo 2,2,1 heptadiene, (norbornadiene), complex $C_7H_8Rh(acac)$, by isomerisation of the triene. However, this has subsequently been shown to be incorrect[6], the diene complex being formed from a 3% norbornadiene impurity in commercial cycloheptatriene.

Green and Kuc[7] have reported that cycloheptatriene reacts rapidly with both bis(bicyclo 2,2,1 heptadiene)rhodium tetrafluoroborate and bis(1,5-cyclooctadiene)rhodium tetrafluoroborate to give crystalline cycloheptatriene complexes. There is some debate as to the mode of bonding of the cycloheptatriene molecule in these complexes. The ^1H N.M.R.



SCHEME of bonding modes in cycloheptatriene metal complexes.



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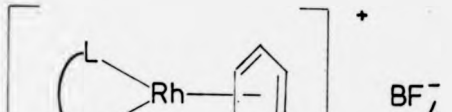

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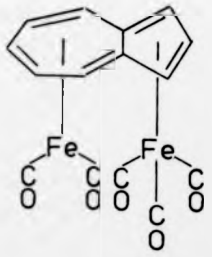


[6]

spectrum indicates 4 resonances associated with the cycloheptatriene ring and this together with double resonance studies leads the authors to the conclusion that the bonding is either 1,2,5,6hapto(h^2,h^2) [4] or 1,2,3,4,5,6 hapto (h^6) [5], the 1,2,3,4 hapto (h^4) form being excluded as this would lead to 1,3 fluxional shifts which, since the spectra are temperature invarient, do not appear to occur. Comparison with the ^{1}H N.M.R. spectrum of h^6 cycloheptatriene molybdenum tricarbonyl leads the authors to the tentative conclusion that the rhodium complexes are also co-ordinated as h^6.

Reaction of platinum compounds with cycloheptatriene results in the formation of complexes with either cycloheptatrienyl or cycloheptatriene moieties. Thus H_2PtBr_6, reacts with cycloheptatriene to give a mixture of ditropyliumhexabromoplatinate $(C_7H_7)_2(PtBr_6)$ and 1,3,5 cycloheptatriene cis-dibromoplatinum II[8]. In the latter compound the mode of bonding of the triene involves 4 electrons since the cycloheptatriene is readily displaced by pyridine to form cis $PtBr_2(C_5H_5N)_2$. However, unlike cycloheptatriene iron tricarbonyl, in which the cycloheptatriene has h^4 co-ordination to the metal, the platinum compound undergoes neither the protonation nor hydride abstraction reactions which normally occur readily with conjugated systems but which do not occur in platinum olefin compounds containing chelating diolefins. This suggests that the mode of bonding in $C_7H_8PtBr_2$ is also h^2, h^2.

With silver, cycloheptatriene can form either 1:2 (Ag:olefin) or 1:1 hydrated complexes, $AgBF_4(C_7H_8)H_2O$ [9]. The exact mode of bonding of the olefin to the metal is not clear, although in the case of the 1:2 complex the number of π electrons in the two cycloheptatriene rings exceeds the electron acceptance capability of the silver ion suggesting that both free and co-ordinated double bonds are present.

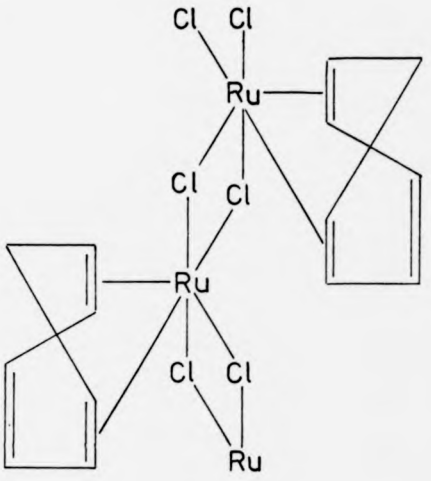
Most of the studies of cycloheptatrienyl and cycloheptatriene transition metal complexes are connected with the group VI metals.

The carbonyl complex $C_7H_8M(CO)_3$, (M=Cr & Mo) is readily prepared by direct reaction of cycloheptatriene with the metal carbonyl $M(CO)_6$. X-ray studies on cycloheptatriene chromium tricarbonyl[10] have shown that for the six olefinic carbon atoms, the c-c bond lengths are virtually equal suggesting that the metal is bonded (h^6) to 6 conjugated π electrons. The methylene protons are out of the plane of the ring and on the opposite side of it to the metal atom. X-ray studies on the analogous molybdenum compound[11] indicate that the mode of bonding is somewhat different to that with chromium in that the c-c bond distances are those expected for alternate single and double bonds of a triene system, as are found in the free olefin, and indicate co-ordination of the metal to 3 isolated double bonds, which might be more accurately represented as h^2,h^2,h^2 rather than h^6. This mode of bonding to molybdenum appears to be much stonger than the bonding of six delocalised electrons in an arene system, since treatment of benzene molybdenum tricarbonyl $C_6H_6Mo(CO)_3$ with cycloheptatriene results in displacement of the benzene ring to produce cycloheptatriene molybdenum tricarbonyl, $C_7H_8Mo(CO)_3$. Also, on reaction of 1-phenylcycloheptatriene with molybdenum hexacarbonyl, $Mo(CO)_6$, it is the C_7H_7ring which bonds to the metal in preference to the arene ring[12].

It is not unreasonable to expect iron to form compounds with cycloheptatriene with a mode of bonding similar to that of the group VI metals i.e. using the six π electrons of the cycloheptatriene ring to attain the inert gas configuration resulting in a compound such as cycloheptatriene iron dicarbonyl where the olefin has h^6 bonding to the metal. Indeed, this mode of bonding could be present in the 7-membered ring of azulenedi-iron pentacarbonyl $C_{10}H_8Fe_2(CO)_5$[13] [6]. However, reaction of cycloheptatriene with iron pentacarbonyl produces not cycloheptatriene iron dicarbonyl but cycloheptatriene iron tricarbonyl

and ^{1}H N.M.R. studies show the cycloheptatriene to be bonded in a conjugated h^4 fashion to the metal[14]. The fact that this mode of bonding is particularly favoured by iron can be shown by reacting iron pentacarbonyl with the non-conjugated 1,5 hexadiene. The product of the reaction contains the conjugated 1,3 hexadiene resulting from isomerisation of the 1,5 form. Similarly, reaction of iron pentacarbonyl with 1,4 cyclohexadiene results in the formation of $(1,3C_6H_8)Fe(CO)_3$[15]. Also, while many transition metals e.g. Mo, W, Rh, Pd and Pt will form complexes with 1,5 cyclooctadiene and reaction with the 1,3 diene results in isomerisation to the 1,5 form, reaction of 1,5 cyclooctadiene with iron pentacarbonyl does not normally form a stable complex but results in isomerisation of the ligand to form the uncomplexed 1,3 diene, presumably resulting from an intermediate complex in which the diene is co-ordinated in an h^4 manner to the metal. This mode of delocalised bonding can also be observed in complexes of iron with butadiene[16] and cyclobutadiene[17]. Presumably it is because of iron having a particular preference for the h^4 mode of bonding, that reaction of iron pentacarbonyl with cycloheptatriene results in the formation of the tricarbonyl rather than the dicarbonyl compound.

In considering the complexes formed between cycloheptatriene and the various transition metals discussed above, it will be seen that while there are a range of complexes in which the olefin is bonded as a triene (h^6) or a conjugated diene (h^4), it does not normally appear to bond as a nonconjugated diene (h^2,h^2). There are few examples of cycloheptatriene acting as a non-conjugated diene. One case in which it does so is the polymeric compound $[C_7H_8RuCl_2]$ formed by reaction of ruthenium trichloride and cycloheptatriene[18], and in which the olefin molecule assumes a boat configuaration with co-ordination between the



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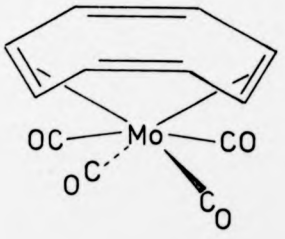

[8]

metal and the 1,5 double bonds [7]. Cycloheptatriene is also bonded in an h^2,h^2 non-conjugated fashion in $C_7H_8PtX_2$(X=Cl,Br). In the first case the mode of bonding is probably influenced by the steric requirements of the polymeric structure while in the latter it is due, to a large extent, to the marked preference of platinum to form spare planar complexes.

This reluctance of cycloheptatriene to act as a non-conjugated diene is in sharp contrast to other, similar, polyolefinic cyclic compounds, which readily bond in an h^2,h^2 fashion to a range of transition metals. Thus, carbonylation of cyclooctatetriene molybdenum tricarbonyl, $C_8H_8Mo(CO)_3$, in which the olefin has h^6 co-ordination to the metal, results in the formation of cyclooctatetraene molybdenum tetracarbonyl $C_8H_8Mo(CO)_4$, in which the olefin is co-ordinated as an h^2,h^2, non-conjugated chelating diene[19] [8]. Treatment of π-$C_5H_5Co(CO)_2$ with cyclo-octatetraene gives the complex π-$C_5H_5CoC_8H_8$ in which the ring acts as a chelating diene. The cyclo-octatetraene molecule is also thought to adopt this mode of bonding in complexes with silver, nickel, rhodium, platium and palladium. However, with iron carbonyl it forms the fluxional h^4 complex $C_8H_8Fe(CO)_3$ which again illustrates the particular preference of iron for this mode of bonding.

Cyclo-octadiene also acts as a non-conjugated chelating diene with a large range of transition metals, e.g. Rhodium, copper, iridium, osmium, nickel, platinum and palladium. Indeed, cyclo-octadiene appears to prefer the non-conjugated form of bonding to the conjugated form, since reaction of 1,3 cyclo-octadiene with rhodium trichloride or group VI metal carbonyls results in isomerisation of the olefin to form cyclo-octa-1,5-diene complexes[20], and it is even possible to isolate the 1,5 isomer of cyclo-octadiene iron tricarbonyl, despite the preference of iron for a conjugated mode of bonding.

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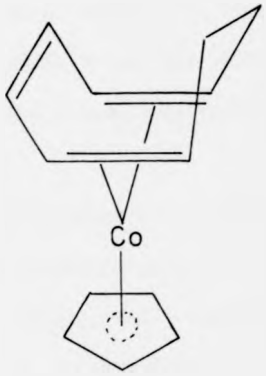

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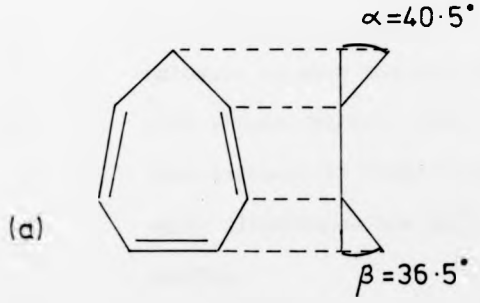

[10]

Cyclo-octatriene will react with cyclopentadienyl cobalt dicarbonyl - π-$C_5H_5Co(CO)_2$, to form the complex $(\pi\text{-}C_5H_5)Co(C_8H_{10})$[21] in which co-ordination of the cyclooctatriene takes place via a pair of unconjugated chelating double bonds [9]. However, this olefin does not appear to form as many h^2,h^2, complexes as either cyclooctatetraene or cyclooctadiene.

It is evident, therefore, that while eight-membered cyclic polyolefin readily form h^2, h^2, non-conjugated chelating bonds to transition metals, cycloheptatriene is much more reluctant to do so, in spite of the fact that in its ring puckering the molecule is very similar to cyclooctatetraene; for cycloheptatriene [10a] $\alpha = 40.5^o$, $\beta = 36.5^o$ while for cyclooctatetraene $\alpha = 42.3^o$[22]. However, while in the eight-membered cyclic polyolefins cyclooctatetraene and cyclooctadiene the 1,2 and 5,6 chelating double bonds are parallel, in cycloheptatriene, the potentially chelating 1,2 and 4,5 double bonds subtend an angle of 27^o [10b] and it may be that the inability of the double bonds to align in parallel planes is a major hinderance to chelation. If so, then this could also explain the comparative reluctance of cyclooctatriene to bond in an h^2,h^2 chelating fashion, while, like cycloheptatriene, it will readily bond in an h^4 or h^6 fashion[23].

Since the only examples of cycloheptatriene acting as a non-conjugated chelating olefin involve complexes in which the metal is either square planar or octahedral, it was thought that rhodium (I), which also favours formation of square planar complexes since it is isoelectronic with Pt(II), might react with cycloheptatriene to form a complex in which the olefin is bonded in an h^2,h^2, non-conjugated fashion.

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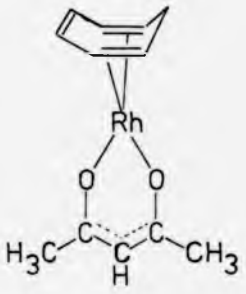

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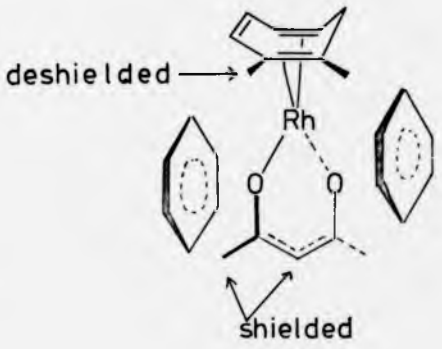

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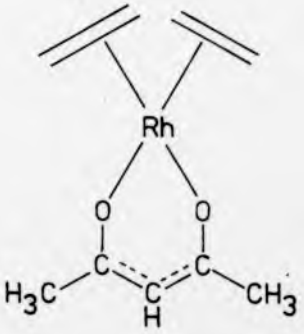

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A. CHEMISTRY

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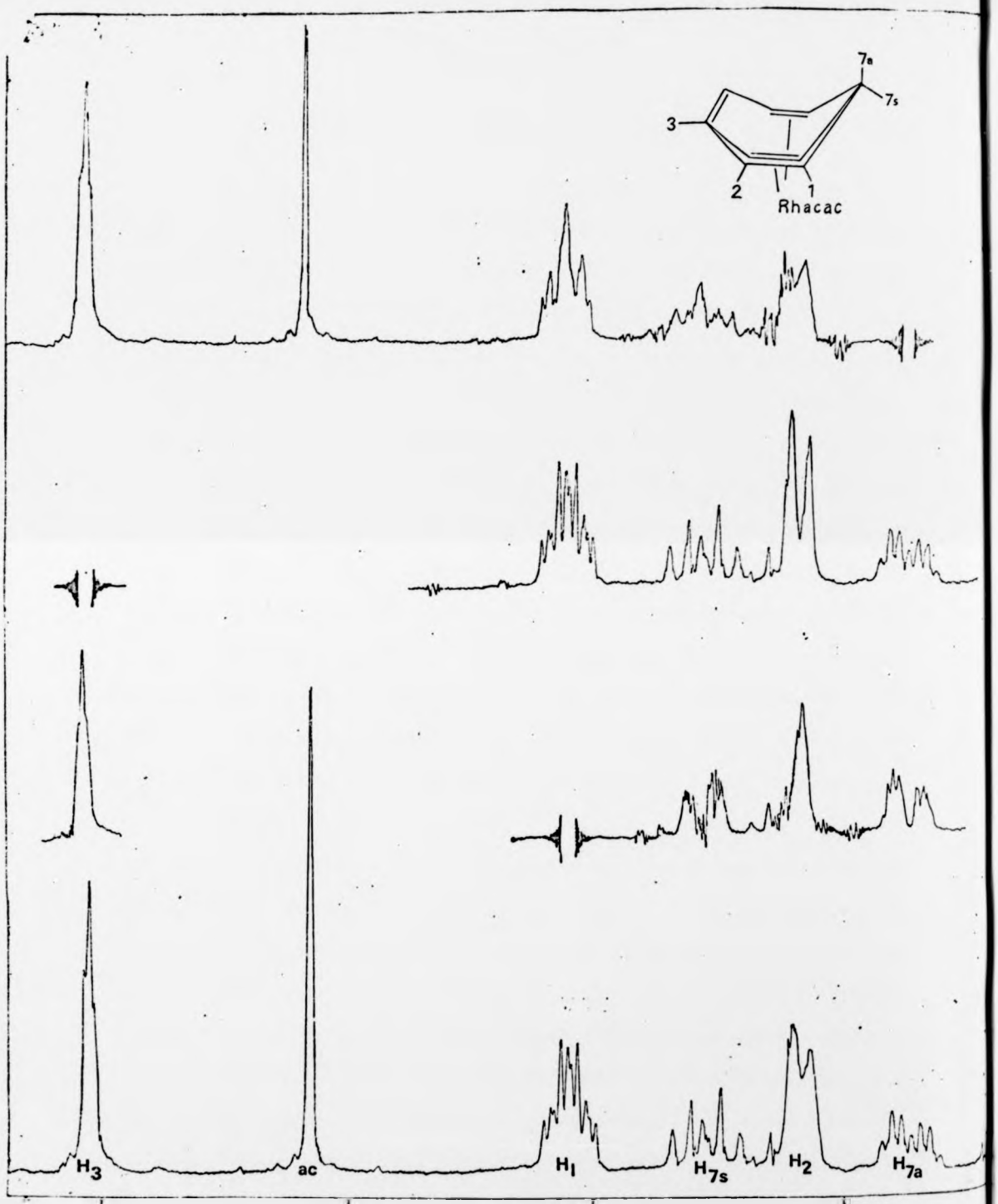
CHAPTER 2

A. CHEMISTRY OF CYCLOHEPTATRIENE RHODIUM ACETYLACETONATE

2A.1 Preparation and Characterisation

North and Rosenblum[1] have reported that cycloheptatriene does not react with dicarbonyl (pentane-2, 4-dionato) rhodium even after reflux at 140°C in a sealed tube for prolonged periods of time. Therefore, in order to produce cycloheptatriene rhodium acetylacetonate, [11], it is necessary to react the cycloheptatriene with a complex of the type (L_2Rh acac) where L is displaced more readily than carbon monoxide. In organometallic rhodium complexes, π bonding is more important than σ bonding[2] and so ligands which have good π acceptor properties will form more stable bonds with the metal. e.g. carbon monoxide; tetrafluoroethylene (C_2F_4); tetracyanoethylene $C_2(CN)_4$. This is why it is thermodynamically unfavourable for cycloheptatriene to displace carbon monoxide from dicarbonyl (pentane-2, 4-dionato) rhodium. In square planar rhodium complexes, the metal has 16 electrons and a vacant p orbital. Substitution reactions take place by an S_N2 reaction involving a 5-coordinate intermediate, formed by σ donation of electrons by the incoming ligand into the vacant p orbital of the metal[3]. This is illustrated by the fact that although, because of its high π acceptor ability, tetrafluoroethylene forms more stable bonds with rhodium than ethylene itself, it only reacts slowly with bis(ethylene) rhodium acetylacetonate [12] due to its relatively poor ability to donate electrons (low nucleophilicity) into the vacant metal p orbital. On the other hand, ethylene, which is a much stronger σ-donor, very rapidly displaces co-ordinated ethylene in [12][2]. This ready displacement makes [12] a particularly useful starting material for the production of cycloheptatriene rhodium acetylacetonate [11]. The latter was obtained as yellow crystals when pure, redistilled cycloheptatriene and bis(ethylene) rhodium (I) acetylacetonate were reacted in ether at 0°C. The combustion



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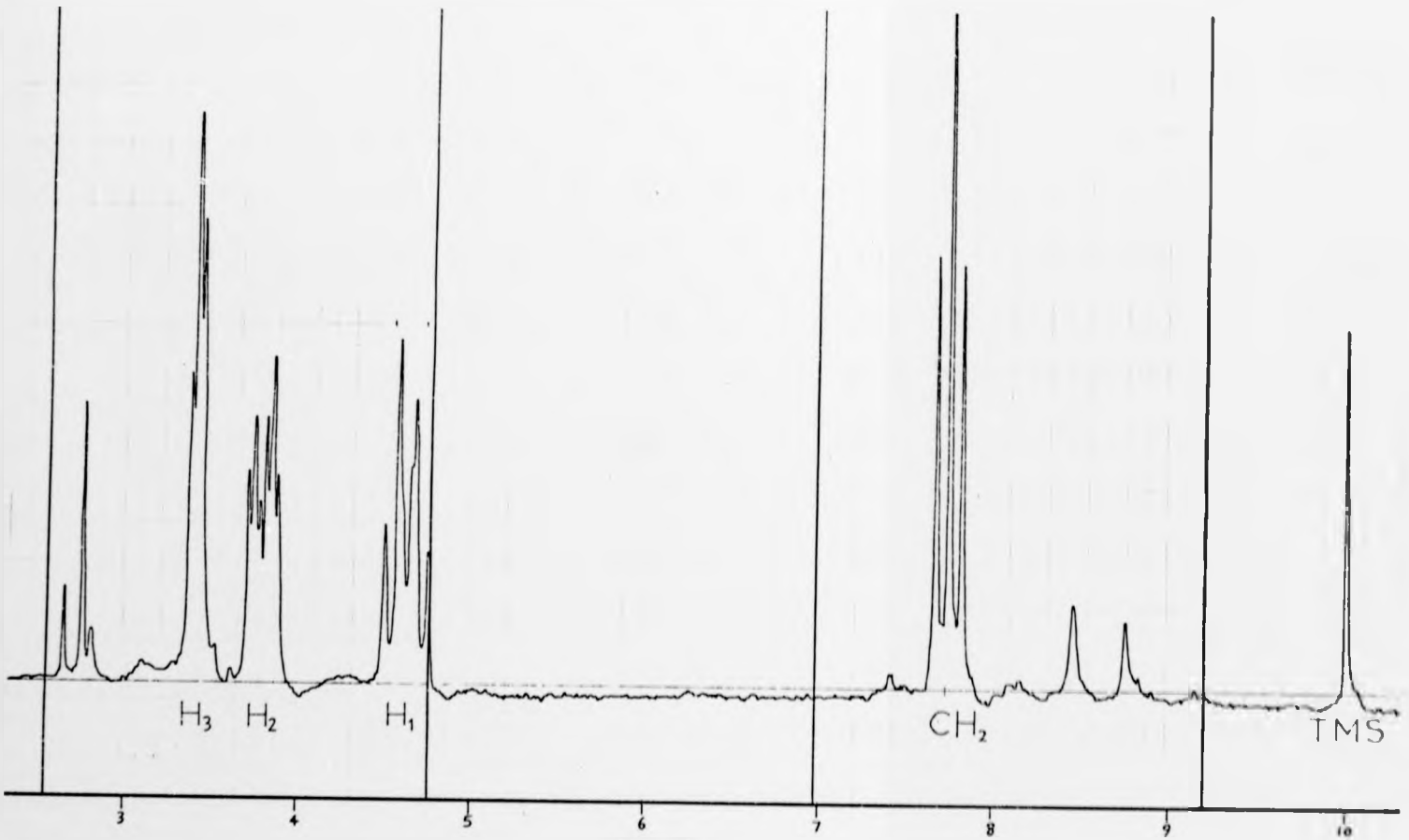

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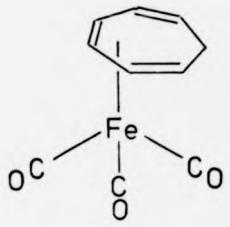

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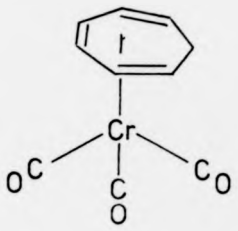

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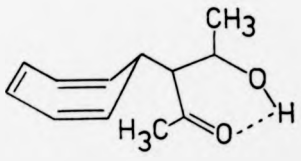

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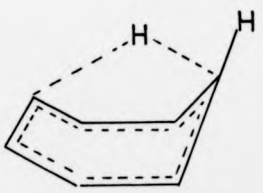

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hydrocarbon
of bonding

analysis is satisfactory, and the ^1H N.M.R. spectrum [13a], clearly indicates that the complex is derived from unrearranged cycloheptatriene; the coupling constants being very similar to those of the parent hydrocarbon [13b]. Thus, for the complex, $J_{1',7\,exo}$ 4Hz, $J_{1',7endo}$ 7.5Hz, $J_{1',1}$ 10Hz, $J_{2',3}$ < 2 Hz, while for free cycloheptatriene the values are 4, 7, 9 and 2 Hz respectively, indicating minimal distortion of geometry on co-ordination to the metal. In establishing that the bonding mode is h^2,h^2, it is worthwhile comparing the spectra of free hydrocarbon and the rhodium complex, with those of cycloheptatriene iron tricarbonyl, $(CHT)Fe(CO)_3$, [14], and cycloheptatriene chromium tricarbonyl, $(CHT)Cr(CO)_3$, [15], in which the modes of bonding are h^4 and h^6 respectively. In the parent hydrocarbon, carbon atoms C_3 and C_4 lie above the plane of C_1, C_2, C_5 and C_6, ($\beta = 36.5^o$)[4]; hence bonding as an unconjugated diene (h^2,h^2) to C_1, C_2, C_5 and C_6 would be expected to cause little or no distortion of the ring, leaving $J_{2',3}$ virtually unchanged, while conjugated bonding as either h^4 or h^6, causes greater distortion which is reflected in larger values for $J_{2',3}$, (7.6Hz for $(CHT)Fe(CO)_3$[5] and 6.97Hz for $(CHT)Cr(CO)_3$[6]). The chemical shift of H_2 upfield with respect to H_1 is the reverse of observations on h^4 and h^6 complexes or the parent hydrocarbon[5,6,7], and the large shifts resulting from shielding of both these protons, (H_1 1·0, H_2 2.79ppm) compared with that of H_3 (0.33ppm), further suggest that it is carbon atoms C_1, C_2, C_5 and C_6 which are bonded to the metal. The chemical shift between the two methylene protons, (0.82ppm), is much larger than that observed in the iron complex, (0.11ppm)[5], and indicates a much stronger interaction between the metal atom and H_{7endo}, than is observed in h^4 complexes. These significant differences in both chemical shifts and coupling constants between [11] and h^4(conjugated diene) and h^6(triene) complexes, together with the small degree of distortion of the hydrocarbon on forming the complex, suggest an h^2,h^2(non-conjugated diene) mode of bonding to the metal.

The chemical shifts using d_6 benzene as solvent were compared with those in deuterochloroform. It was found that in benzene, protons H_1 and H_2 were shifted downfield (deshielded) by 0.17 and 0.35ppm respectively while the signals of H_3 and acetylacetonate were all shifted upfield by 0.05 ppm. Fig. [11a] illustrates an interaction between the complex and solvent which would result in this effect.

The interpretation of the N.M.R. spectrum was facilitated by the use of double resonance, (see [13a]).

2A:2 Reaction of [11] with (i) triphenylmethyl tetrafluoroborate ($Ph_3C^+BF_4^-$), and (ii) diazomethane (CH_2N_2)

In view of the known ability of h^4 bonded[8] and h^6 bonded[9] cycloheptatriene to undergo reaction with triphenylmethyl tetrafluoroborate, resulting in addition of the triphenylmethyl cation across the free double bond in h^4 and hydride abstraction to produce the tropylium ion in h^6, the reaction between triphenylmethyl tetrafluoroborate and cycloheptatriene rhodium acetylacetonate [11] was also investigated. Neither hydride abstraction nore addition to the double bond occurred when a solution of triphenylmethyl tetrafluoroborate was added to [11] in ether, although considerable darkening occurred. Instead, fractional crystallisation from pentane yielded unchanged starting material.

Similarly, reaction of [11] with excess diazomethane in ether resulted in decomposition of the complex rather than addition to the double bond. No evolution of nitrogen was observed. These results further suggest that the hydrocarbon is bonded in an h^2,h^2 fashion to the metal, since dichloro(cycloheptatriene)platinum (II), which also has an h^2,h^2 mode of bonding, undergoes neither hydride abstraction nor protonation reactions[10].

2A:3 Decomposition of [11] in deuterochloroform

Although stable in hydrocarbon solvents to 90°C, [11] is degraded after eight hours at 60°C in deuterochloroform. Subsequent washing with cyanide ion and drying over anhydrous magnesium sulphate produced acetylacetonylcycloheptatriene [16][11] in low yield. The product was identified by comparing its N.M.R. spectrum with that of acetylacetonylcycloheptatriene and by mixed melting point at 124°C.

2A:4 Hydrogen shifts in cycloheptatriene rhodium acetylacetonate

Free cycloheptatriene has been shown[12] to undergo a thermal (1,5) hydrogen migration. This is thought to proceed via a transition state [17] in which the migrating hydrogen is simultaneously bonded to both carbon atoms[13], thus involving specific exo-migration.

Cycloheptatriene complexed to the Group VII metals chromium and molybdenum, undergoes far more rapid sigmatrophic hydrogen shifts than the parent hydrocarbon and in contrast to the latter, has been shown to involve specific endo-migration, since while 7-exo-substituted cycloheptatriene complexes undergo rearrangements, the 7-endo-substituted complexes do not[14,15]. The mechanism has been shown to involve a (1,5) hydrogen shift[16] and not, as was originally postulated[14], an intermediate tropylium metal hydride species. We therefore decided to investigate the possibility of a similar reaction occurring in [11].

Hydrogen nuclei in different chemical surroundings may have their N.M.R. chemical shift positions averaged by exchange phenomena. Thus, if the exchange is considerably more rapid than the difference between the two chemical shifts in Hz, then only one sharp resonance is observed midway between the separate chemical shift positions. However, such a rapid isomerisation does not occur in [11], since no change was observed in the N.M.R. spectrum up to 85°C. Therefore, in order to investigate a

TABLE 1

Deuterium migration in $C_7H_8Rh(1)acac$ at 60°C.

	Number of hydrogen atoms at:			
	$C_{1,6}$	$C_{2,5}$	$C_{3,4}$	$C_{7exo} + C_{7endo}$
Initial	2.00	2.00	1.95	1.07
60°//30min	1.99	1.98	1.61	1.42
60°//90min	1.97	1.82	1.81	1.41
60°//1080min	1.62	1.78	1.73	1.86
Recovered CHT	1.63	1.72	1.75	1.90

TABLE 2

Deuterium migration in $C_7H_8Rh(1)acac$ at 75°C

	Number of hydrogen atoms at:				
	$C_{1,6}$	$C_{2,5}$	$C_{3,4}$	C_{7endo}	C_{7exo}
Initial	1.89	2.00	2.00	0.50	0.37
75°//31min	1.88	1.93	1.87	0.56	0.52
75°//52min	1.81	1.86	1.84	0.66	0.59
75°//78min	1.78	1.80	1.77	0.74	0.67

slower exchange, the analagous mono-deutero compound was prepared from 7-(^{2}H)-cycloheptatriene, which was itself prepared from tropylium tetrafluoroborate ($C_7H_7BF_4^-$) and lithium aluminium deuteride ($LiAlD_4$). The exchange reaction was monitored by N.M.R. at 60°C (Table 1) and at 75°C (Table 2), by determining the deuterium distribution from the relative intensities of the ligands N.M.R. resonances. The data for the 60°C experiment, (obtained by duplicate tracings and weighings of the Perkin-Elmer R12, 60MHz N.M.R. spectrum) appears to indicated a non random distribution with most of the deuterium appearing initially at $C_{3,4}$ in keeping with a 1,5 shift[19]. However, the margin of error involved in this method is considerable, so in order to achieve a more accurate result, the migration at 75°C was monitored on a Bruker 90MHz N.M.R. spectrometer, which has the advantage of greater separation of signals and automatic calculation of resonance intensities. The data from this experiment, (Table 2), shows that, within the limits of experimental error, the rate of deuteration at each carbon atom is the same, indicating completely random distribution. In the initial phase of the reaction, both at 60°C and at 75°C, 7-exo-protium appears to grow faster than 7-endo-protium, which is in keeping with selective endo-migration. However, since 7-endo-protium is greater than 0.5 atom and recovered cycloheptatriene contains less than 0.5 atom of deuterium at C_7, it is inferred that the overall selectivity is masked by exchange with traces of free cycloheptatriene in the sample resulting in loss of stereochemical memory.

The completely random distribution of deuterium in this case contrasts with the migration in both free cycloheptatriene and its complexes with the Group VII metals, chromium and molybdenum, where a 1,5 shift occurs[16]. As with the Group VII metal complexes, the migration in [11] is much faster than in the free hydrocarbon and appears to be endo specific rather than exo.

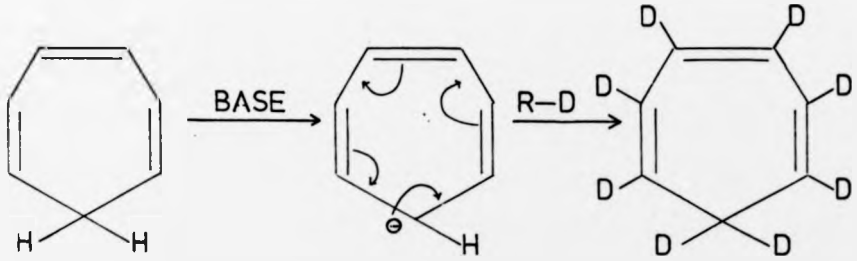
n atoms at:

$C_{7exo} + C_{7endo}$
1.07
1.42
1.41
1.86
1.90

n atoms at:

do	C_{7exo}
	0.37
	0.52
	0.59
	0.67

[18]



[SCHEME 1]

Since the distribution is random, however, a different intermediate species is obviously involved. This could well be π-allyl rhodium hydride, [18], where fast valence tautomerism would result in random reprotonation, and the structure of the intermediate would favour specific endo migration.

2A:5 Base catalysed deuteration of cycloheptatriene

In order to attempt to define more clearly the course of hydrogen migration in cycloheptatriene rhodium acetylacetonate [11], an attempt was made to prepare the heptadeutero analogue $(C_7D_7H)Rh$ acac from perdeutero cycloheptatriene (C_7D_8).

Production of the d_8 compound was first attempted using base catalysed deuteration of cycloheptatriene. It has been shown[17] that whilst cycloheptatriene does not react in 10% methanolic sodium methoxide after 24 hours at 110°C, reaction with a stronger base, in the presence of a source of exchangeable deuterium, results in deuteration of the cycloheptatriene by a mechanism involving generation of the cycloheptatrienide anion, $(C_7H_7^-)$[17], (See Scheme 1). Reaction of cycloheptatriene with deuterated triethylcarbinol containing 5g of reacted potassium for 12 hours at 115°C produces 55.9% octadeutero cycloheptatriene[17]. Since a much higher yield, (> 90%d_8), was required for the production of $(C_7D_7H)Rh$ acac, attempts were made to increase the yield by modifying the procedure.

The initial attempt involved heating cycloheptatriene with a molar solution of potassium t-butoxide in hexadeutero-dimethyl sulphoxide at 75°C until exchange equilibrium had been reached, (90 seconds monitored by N.M.R.), followed by addition of D_2O to quench the reaction and removal of the upper, cycloheptatriene layer. Successive repetitions of this process eventually produced 95% d cycloheptatriene. However, the overall yield for the reaction is very small (< 10%), due to formation

of polymer, (see Scheme 3). Since the polymeric compounds are conjugated, they are capable of forming very stable anions and, therefore, once produced they will react readily with further cycloheptatriene. Studies of the reaction using proteo dimethyl sulphoxide have shown that the tendency to polymerise is increased each time the reaction is repeated as the upper layer invariably contains some polymer, in addition to cycloheptatriene, resulting in the percentage of recovered cycloheptatriene decreasing more rapidly with each successive pass. Thus, after one pass, 60% of starting material was recovered, while after two passes, this was reduced to 18%.

In an attempt to decrease this effect, the cycloheptatriene was distilled off after each pass. This process was very time consuming, each distillation taking up to 3 hours by long path trap-to-trap method and only succeeded in producing a 50% yield at each pass.

A second modification attempted to improve the yield by diluting the reaction mixture and so decreasing the polymerisation reaction. Thus, the reactants were diluted with hexamethylphosphoramide, (H.M.P.A.- $[(CH_3)_2N]_3PO$), to give H.M.P.A./D.M.S.O. in the ratio of 4:1 by adding a solution of cycloheptatriene in d_6 D.M.S.O. to a molar solution of potassium tertiary butoxide in H.M.P.A.

Monitoring by N.M.R., the reaction was carried out over both a range of reaction times and temperatures in order to find the optimum conditions where exchange was maximised while minimising the polymerisation reaction. This was found to occur when reacting for 40 seconds at $75^{o}C$, (80% recovered cycloheptatriene).

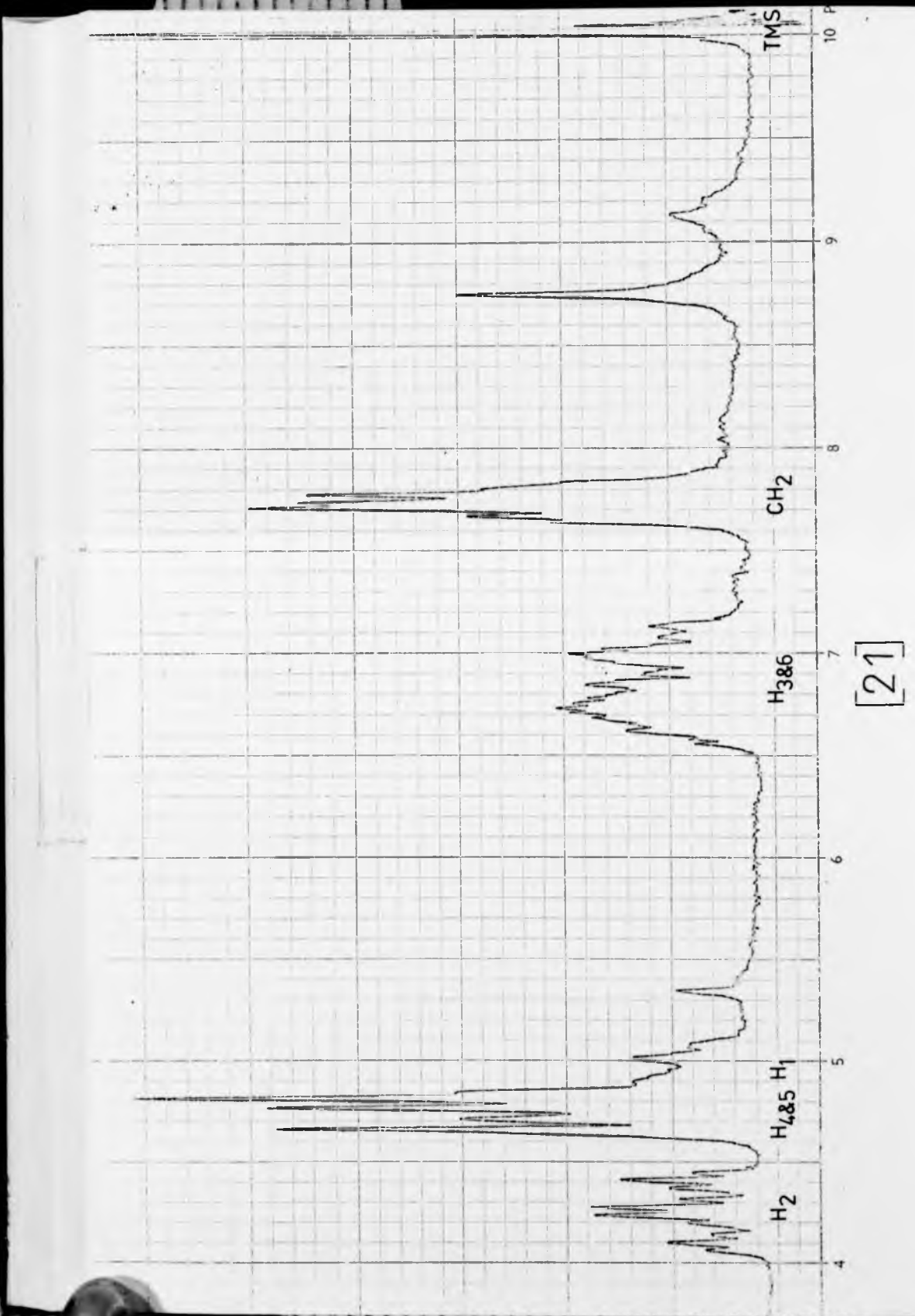
It has been reported[18] that the cycloheptatrienide ion is deep blue in solution. However, in the above reactions, the solution is initially a cherry red colour and only becomes blue during the course of the exchange reaction. We suggest therefore, that the monomeric

[SCHEME 3]

cycloheptatrienide ion, (which is only present in low concentration due to the equilibrium with cycloheptatriene), is in fact red in solution and that conversion to blue is due to the increasing concentration of blue polymeric anion in the solution. Subsequent work has shown[20] that when cycloheptatriene is added to 0.7M potassium amide in liquid ammonia at -33°C a deep red-brown colour is produced due to the presence of the dimer, tricyclo $\left[7,4,1,o^{2,8}\right]$tetradeca - 3,5,10,12-tetraen-7-yl potassium, [20], which is thought to be formed via a cycloheptatrienide ion intermediate, (Scheme 3). This supports the view that the blue colour increases with the degree of polymerisation since the latter will increase the conjugation in the molecule, resulting in a bathochromic shift and a consequent increase in the amount of light of shorter wavelength transmitted. Hence the dimeric anion is red-brown while the monomer is cherry red.

While the reaction in dilute solution succeeded in producing a much higher recovery rate for cycloheptatriene at each pass, the fact that the reaction had to be repeated several times to produce a satisfactory level of deuteration, together with the lengthy extraction procedures necessary at each step, made this a rather unsatisfactory method for obtaining reasonable quantities of $\left[^2H_8\right]$-cycloheptatriene. Despite this low yield, it was possible to prepare $\left[^2H_7\right]$-tropylium tetrafluoroborate, on a small scale, by reacting $\left[^2H_8\right]$-cycloheptatriene with triphenylmethyl tetrafluoroborate, ($Ph_3C^+BF_4^-$). The yield of tropylium ion was greatly increased by using acetic anhydride rather than acetone as solvent. Control experiments on $\left[^1H_7\right]$-tropylium tetrafluoroborate showed that in the generation of cycloheptatriene from tropylium ion, using $NaAlH_2(OCH_2CH_2OCH_3)_2$ - (70% in benzene solution) as proton donor rather than $NaBH_4$ or $LiAlH_4$ gave a much higher yield, making this a much more suitable route for the preparation of C_7D_7H from the limited amounts of $\left[^2H_8\right]$-

cycloheptatriene produced in the base-catalysed deuteration reaction.



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B. PROTON EX

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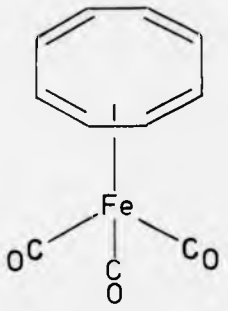
B. PROTON EXCHANGE IN CYCLOHEPTATRIENE IRON COMPLEXES

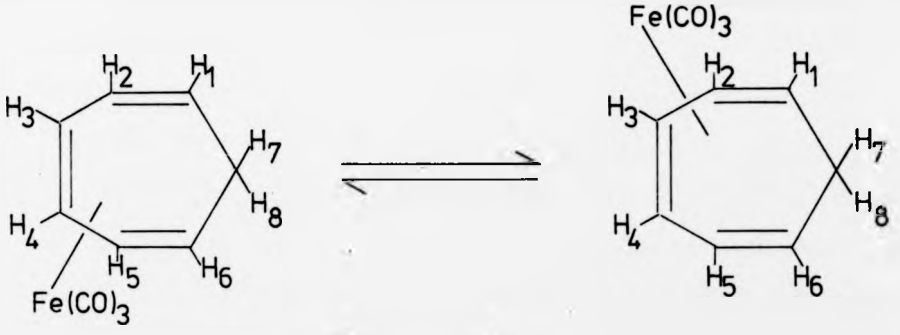
Maltz and Kelly[21] have shown that when cycloheptatriene iron tricarbonyl [14] is treated with 10% sodium methoxide in deuteromethanol for one hour at room temperature, exchange occurs, giving complex which is 6% [$^2H_0$], 93% [$^2H_1$] and 1% [$^2H_2$] with deuteration occurring selectively at the 7-exo position. They also note that at longer reaction times the degree of deuteration is increased. The deuteration at positions other than 7-exo presumably proceeds by sequential exchange and hydrogen shift and if this was non-stereospecific then it would provide a convenient route for the synthesis of [$^2H_8$] cycloheptatriene.

2B:1 Preparation of Cycloheptatriene iron tricarbonyl [14]

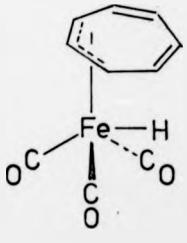
The preparation of [14] was achieved by refluxing cycloheptatriene with tri-iron dodecacarbonyl in heptane, followed by distillation and chromatography. The N.M.R. spectrum in perdeuteromethanol [21] was consistent with that reported for the compound by other workers (5) and indicates a conjugated, (h^4), mode of bonding to the metal. The resonances of the unconjugated double bond are inequivalent and occur at τ 4.25 (H_2, $J_{1,2}$ 10.6Hz, $J_{2,3}$ 7.7Hz), and 4.85 (H_1), the latter being partly hidden by the resonance centred at 4.76 τ due to the two equivalent protons, H_4 and H_5 ($J_{4,5}$ 4.74Hz). The terminal protons of the conjugated double bond are inequivalent and resonate at τ 6.70 (H_3) and 7.04 (H_6), whilst the methylene protons, which will be in slightly different chemical environments and therefore non-equivalent, give rise to the multiplet centred at 7.7 τ. Running the spectrum in d_6 benzene rather than d_4 methanol results in an upfield shift for all resonances; protons H_4 and H_5 having the greatest shift (0.57p.p.m.), [30a] . This suggests association of a benzene molecule with the ligand in preferential face-to-face orientation so that its ring protons lie within the shielding cone of the



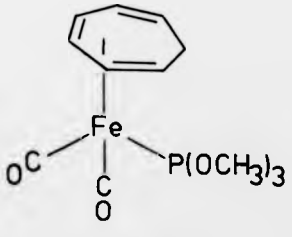
[22]



[SCHEME 4]



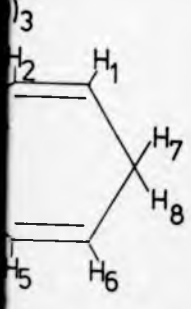
[25]



[26]

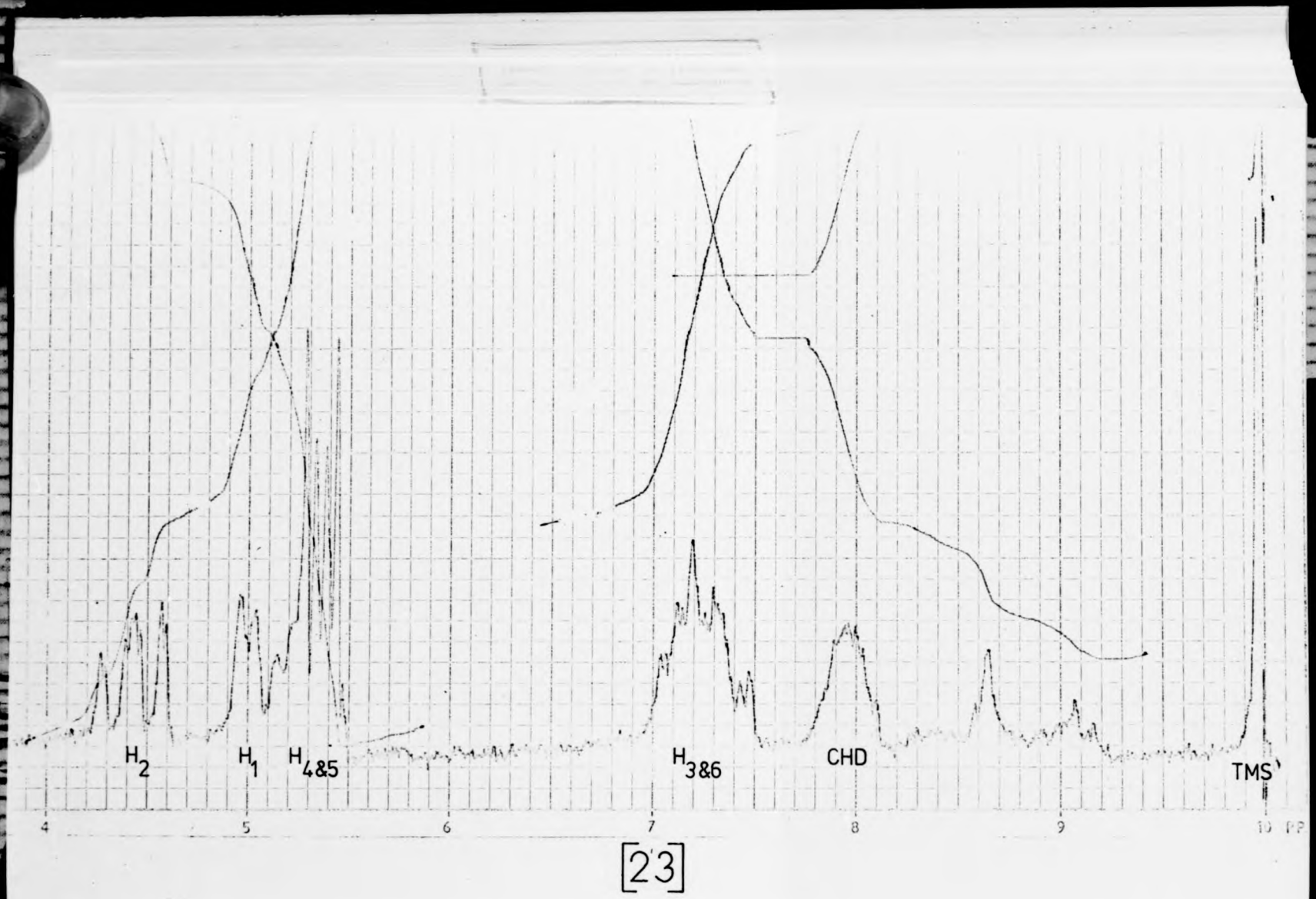
aromatic ring. Similar examples have been noted by Dr. K.R. Aris (Ph.D. thesis, Warwick University, 1972).

Since cyclooctatetraene iron tricarbonyl [22], exhibits rapid fluxional behaviour[22], we decided to investigate [14] in order to see whether a similar property was exhibited here also. If the fluxional behaviour depicted in Scheme 4 occurs at a reasonable rate, then irradiation of the ^1H N.M.R. signal at H_1 should result in a decrease in signal strength at H_6 and vice versa due to spin saturation transfer. The same is also true for protons H_2/H_5 and H_3/H_4. However, the spectral data for [14] in d_6 benzene, show no evidence for a decrease in signal strength of complementary protons on decoupling and thus it appears that, at the normal operating temperature of the N.M.R. probe, (33°C), the molecule does not exhibit fluxional behaviour but has instead a static structure. Similar experiments carried out with cycloheptatriene iron dicarbonyl trimethyl phosphite, $C_7H_8Fe(CO)_2P(OCH_3)_3$, [26] indicated that this molecule also has a static structure. N.M.R. spectra of [14] taken with probe temperatures of 94° and 104°C show no line broadening, indicating that the molecule does not exhibit fluxional behaviour even at elevated temperatures.

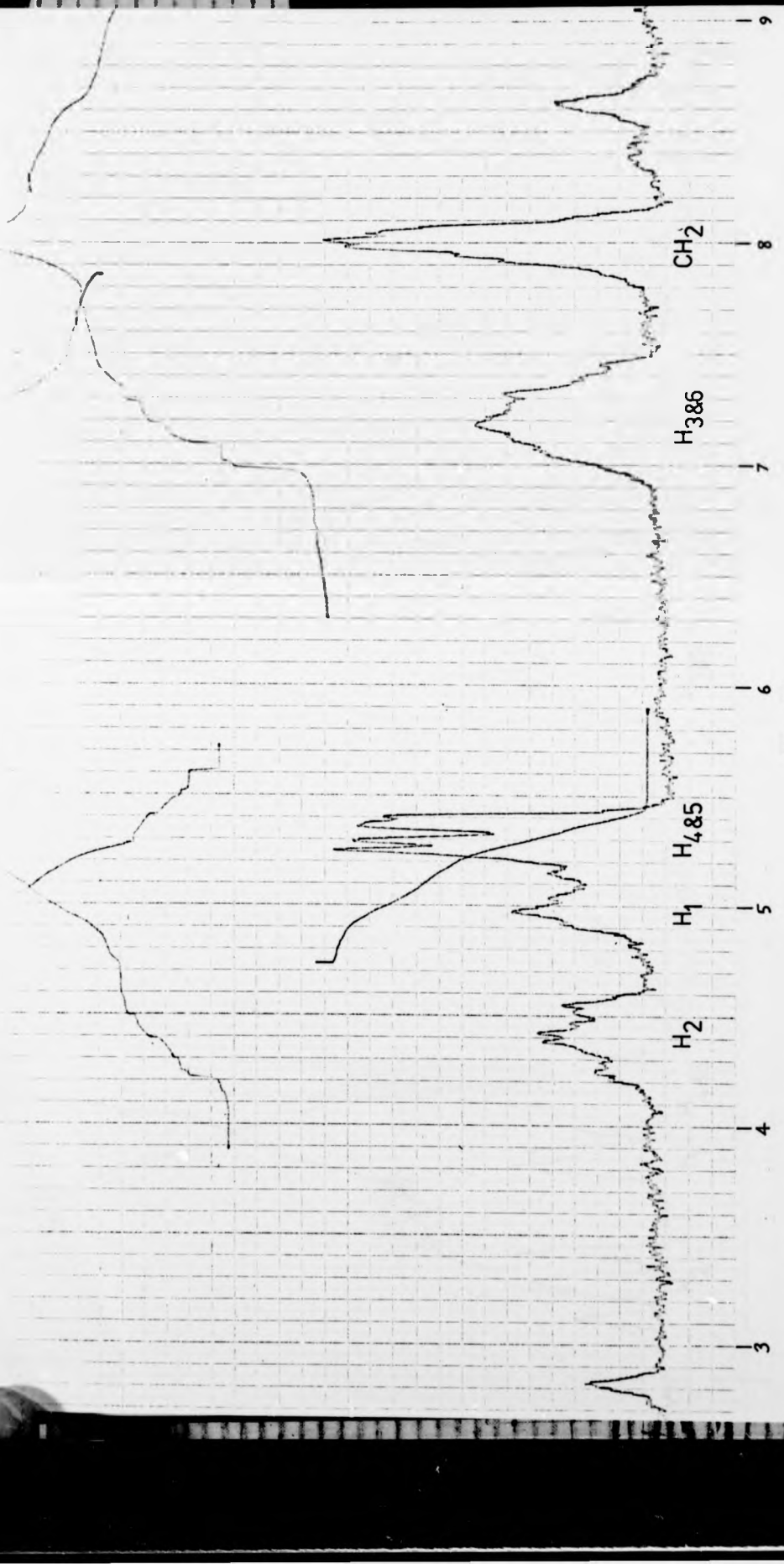


2B:2 Base-catalysed, hydrogen-isotope exchange in cycloheptatriene iron tricarbonyl [14]

When a small amount of potassium t-butoxide was added to [14] in d_6 dimethyl sulphoxide the solution turned deep red due to the generation of the anion $C_7H_7Fe(CO)_3^-$, identified by its N.M.R. spectrum, (sharp singlet at 5.35)[1]. The anion was also generated with 1M potassium t-butoxide in HMPA. An N.M.R. spectrum taken in molar $KOBu^t$/HMPA indicated that there was no equilibrium between the anion and the neutral species - the spectrum showed only the anion as a sharp singlet at 5.35τ. Addition of perdeuteromethanol, (CD_3OD) caused the anion to



[23]



[24]

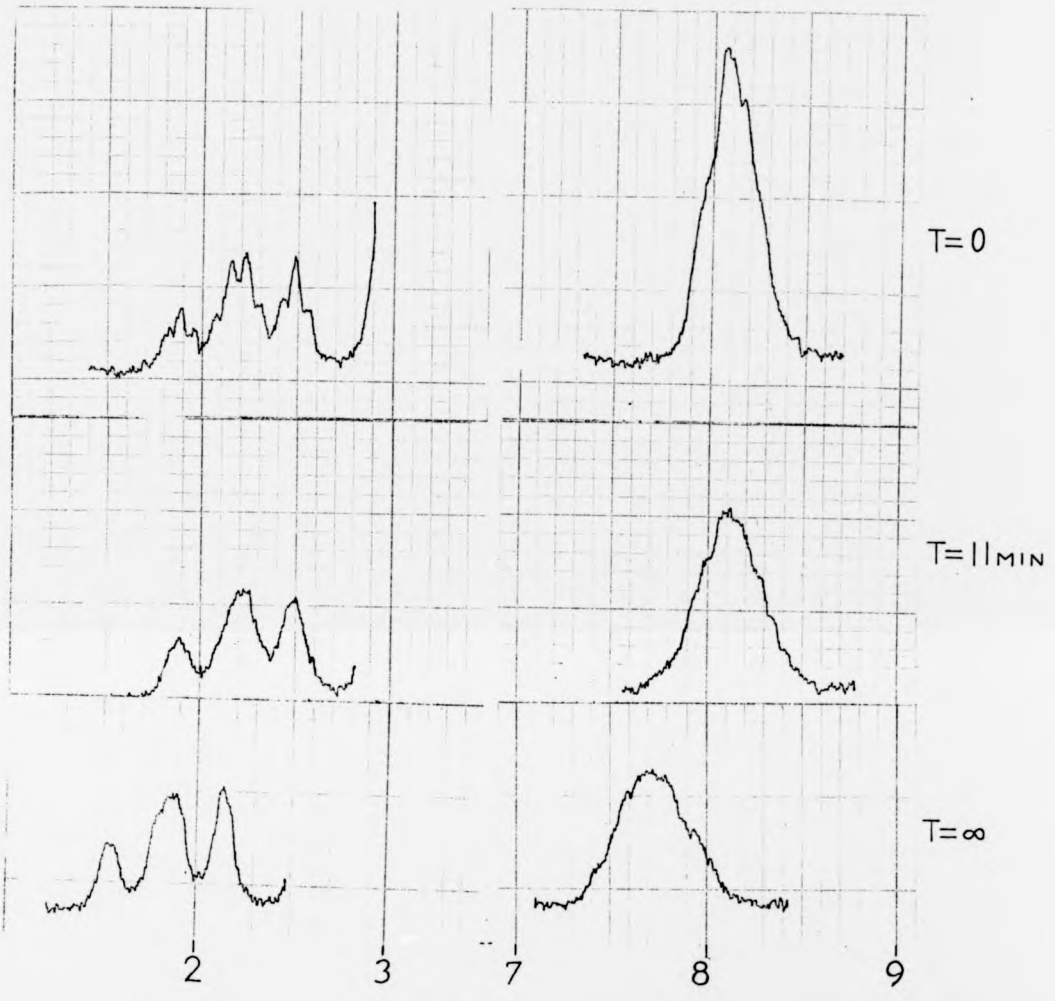
be quenched producing 7-[$^2H_1$] - cycloheptatriene iron tricarbonyl.

It was found that at room temperature only the exo-hydrogen was exchanged, [23]. However, on heating the product for up to one hour at 100°C in benzene, scrambling occurred, resulting in the distribution of the deuterium over seven of the eight ring positions, the endo-hydrogen being unaffected, [24]. Thus it was thought that it would be possible to form [$^2H_7$] -cycloheptatriene iron tricarbonyl, ($C_7D_7HFe(CO)_3$), in one step by carrying out the exchange reaction at 100°C. Anomalous results were obtained with H.M.P.A. as solvent, so the reaction was carried out in 0.8 molar [$^2H_3$] -sodium methoxide in [$^2H_4$] -methanol, for 30 minutes at 120°C in a sealed N.M.R. tube. During the course of the reaction some decomposition occurred in the tube. The N.M.R. spectrum showed a decrease in the intensity of the proton resonances of [14] and after treatment for three successive 30 minute periods these were only about 8% of their initial values. This was at first thought to be due to deuteration but subsequent infra-red data showed that although some deuterated material had been produced, for the most part the complex had merely decomposed.

It would appear that, although the methoxide-catalysed deuterium exchange occurs rapidly, and [$^2H_1$] -cycloheptatriene iron tricarbonyl readily scrambles to distribute the deuterium around the ring, the latter reaction does not occur in the presence of base - possibly because at the high temperature used, the base either causes decomposition, or alternatively, itself reacts with the complex.

In an attempt to overcome the need for high temperature, an experiment was carried out in order to see whether photolysis of [$^2H_1$] -cycloheptatriene iron tricarbonyl would cause scrambling. However, after 5 hours no scrambling had occurred and free cycloheptatriene was detected in the reaction mixture.

Since, on scrambling, the endo-hydrogen is unaffected, the intermediate formed in this reaction is probably the metal hydride species $(C_7H_7)HFe(CO)_3$, [25].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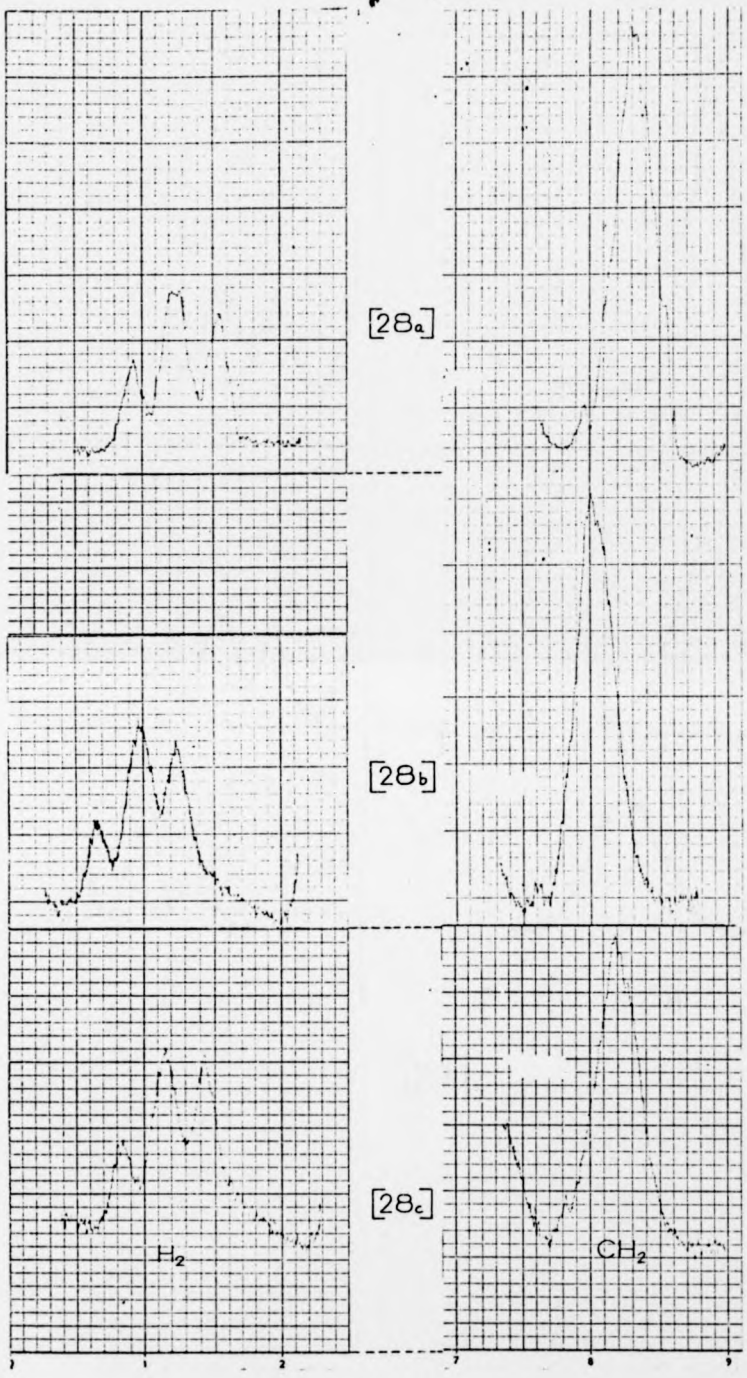
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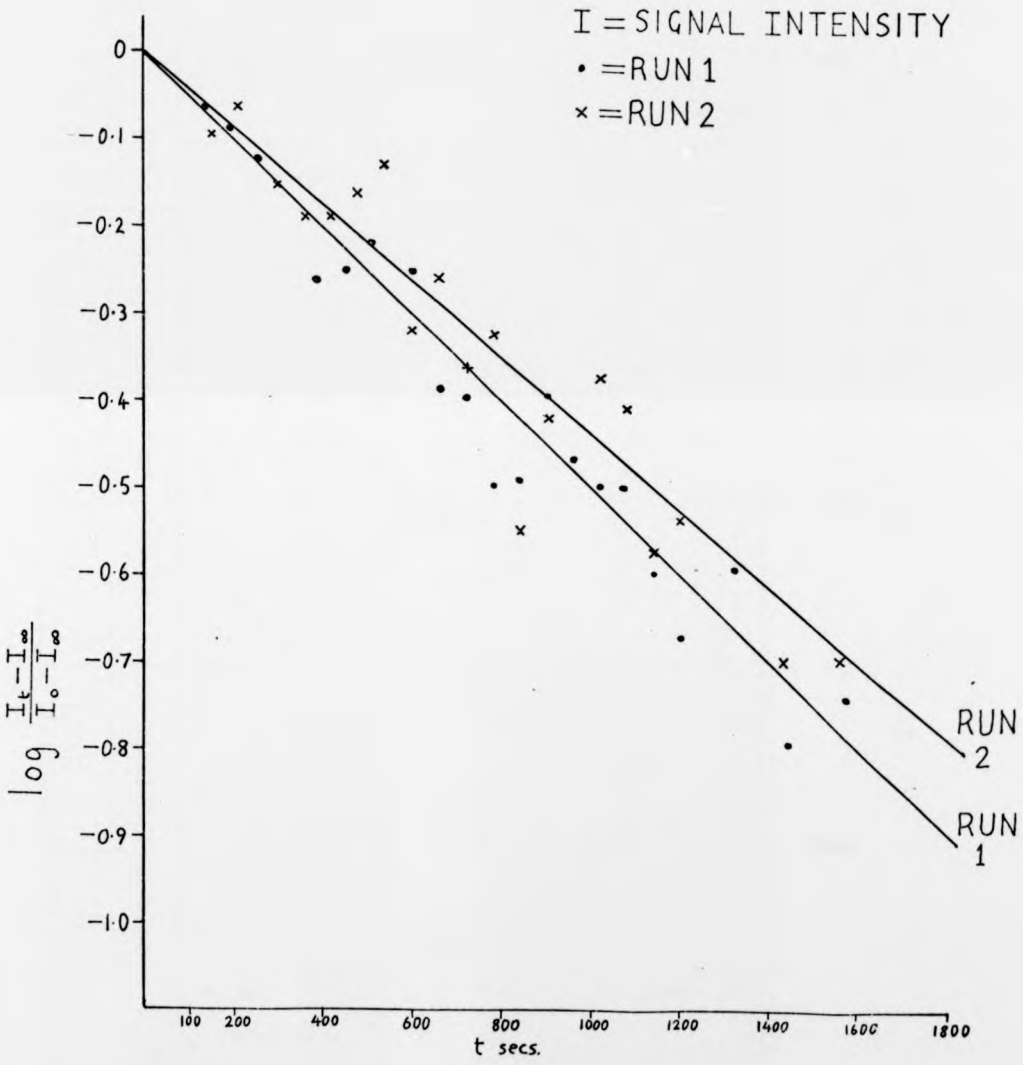
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TABLE 3

Rates of deuterium exchange in $C_7H_8Fe(CO)_2L$. (L = CO, $P(OCH_3)_3$).

	$C_7H_8Fe(CO)_3$		$C_7H_8Fe(CO)_2P(OCH_3)_3$	
	Run 1	Run 2	Run 1	Run 2
Rate constant $k(sec^{-1})$	2.2×10^{-4}	1.9×10^{-4}	8.4×10^{-6}	9.0×10^{-6}

2B:3 Kinetic Studies

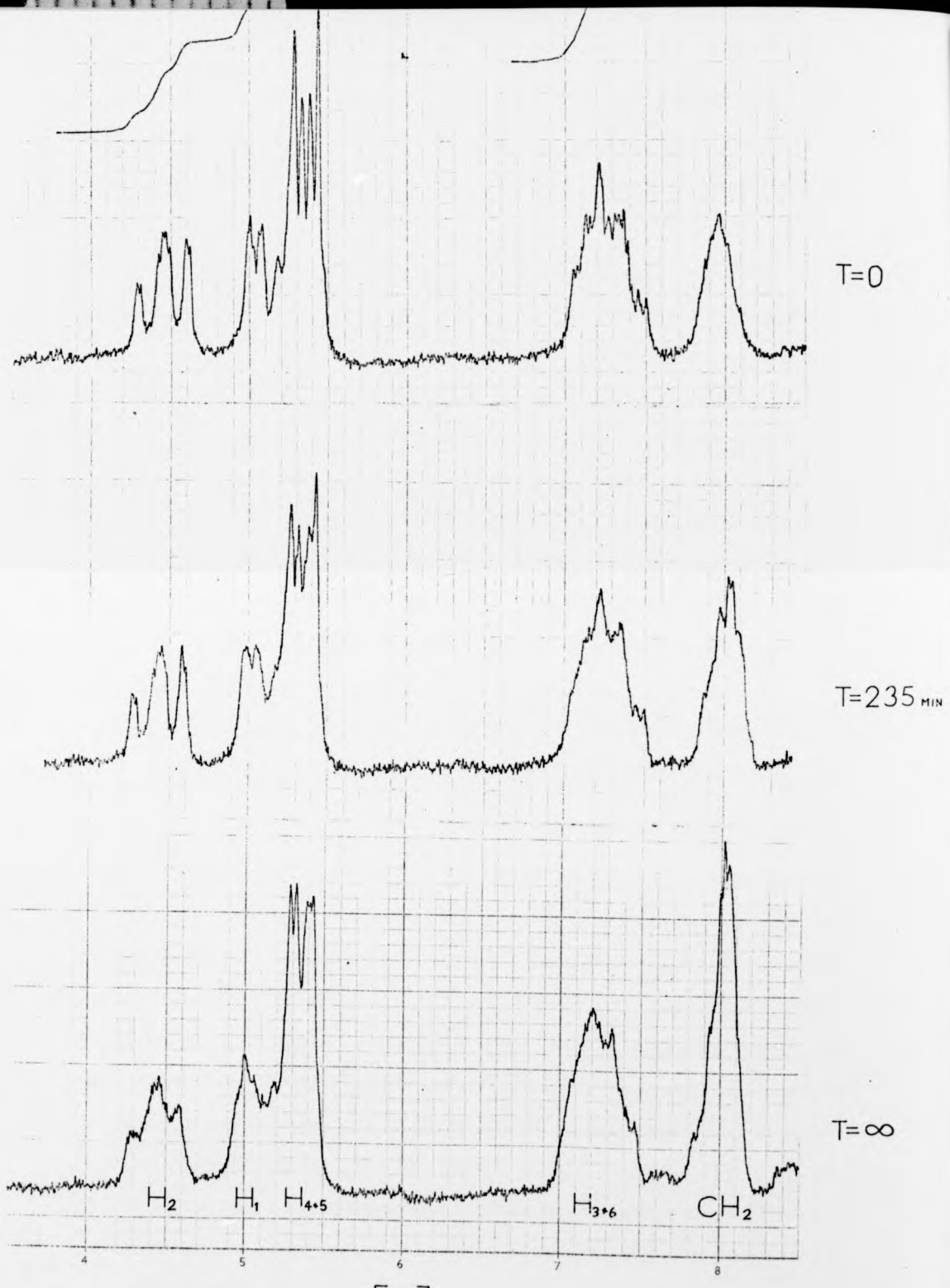
If the intermediate in the scrambling reaction is [25], then replacement of one of the liganded carbonyl groups by a stronger Lewis base might result in stabilisation of this hydride intermediate and therefore a lowering of the temperature required for scrambling to occur, or conversely, an increase in the rate of scrambling at a given temperature. At the same time, the increased negative charge on the metal may destabilise thecycloheptatrienyl anion formed in the base-catalysed exchange, resulting in a decrease in the rate of this reaction. We, therefore, decided to compare the rates of base-catalysed deuterium exchange and deuterium scrambling in both cycloheptatriene iron tricarbonyl and cycloheptatriene iron dicarbonyltrimethylphosphite, [26]; the latter compound being prepared by heating cycloheptatriene iron tricarbonyl with trimethylphosphite at 60°C for several days.

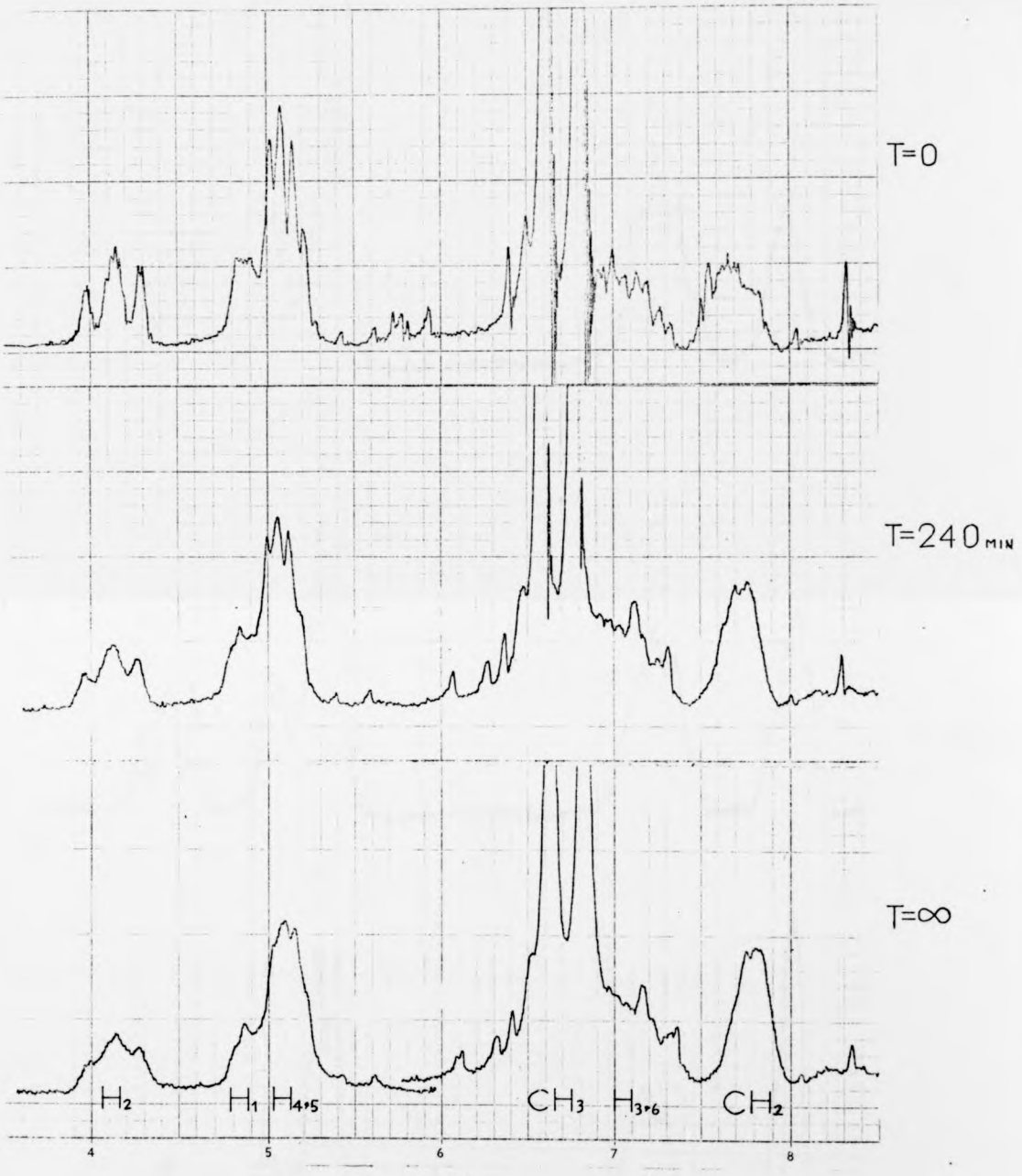
The reactions were followed by observing the degree of deuteration, indicated by the relative intensities of the N.M.R. resonances. These were calculated by duplicate tracings and weighings of the peaks.

2B:3.1 Exchange reactions

Deuterium exchange was carried out in 0.435M [$^2H_3$] -potassium methoxide in [$^2H_4$] -methanol. Since the only exchangeable proton was 7-exo, the degree of deuteration at time t was determined by comparing the relative intensities of the $-CH_2$ resonance at 7.7τ with that of the non-exchangeable one proton resonance at 4.25 τ (H_2). This method also has the advantage of eliminating much of the error due to fluctuations in the spectrometer. The relative intensities of the peaks at t_o, $t_{\frac{1}{2}}$ (approx) and t_∞ are shown in figs. [27], ($C_7H_8Fe(CO)_3$) and [28] ($C_7H_8Fe(CO)_2P(OCH_3)_3$).

The first order rate plots for two separate runs on cycloheptatriene iron tricarbonyl [14] are very similar, [29] and the rate constants (Table 3), are much larger than those of the phosphite complex [26], which again are consistent and which were computed from the results using


T=0
T=235 MIN
T=∞
H2
H1
H4+5
H3+6
CH2
4
5
6
7
8



[31]

RELATIVE INTENSITY
0·5
0·4
0·3
0·2
0·1
0
100 200 300 400 500 600 700 800 900
t MIN
[32]
•= SIGNAL A
o= SIGNAL C
×= SIGNAL B
▲= SIGNAL D
0·5
0·4
0·3
0·2
0·1
0
100 200 300 400 500 600
t MIN
[33]

a least squares plot of the first order rate equation. This indicates that, as expected, the rate of exchange is very much faster in the tricarbonyl complex ($t_{\frac{1}{2}}$ = 640 secs) than in the phosphite ($t_{\frac{1}{2}}$ = 14800 secs). Clearly the superior σ-donor qualities of trimethylphosphite relative to carbon monoxide inhibit the formation of an anionic intermediate.

An attempt was made to follow the exchange reaction in cycloheptatriene iron dicarbonyltriphenylphosphine but deuteration of the ring was extremely slow, thus making impracticable a kinetic study by this method. However, it does illustrate further the inhibiting effect of strong σ-donor ligands.

2B:3.2 Deuterium Scrambling

On heating at 75°C in d benzene, extensive scrambling occurred in both $(C_7H_7D)Fe(CO)_3$ and $(C_7H_7D)Fe(CO)_2P(OCH_3)_3$. The N.M.R. spectra, [30] and [31] respectively, show the relative intensities of the peaks at t_o, t_x and t_ω. From these spectra it would appear that the rate of scrambling is somewhat faster in the phosphite complex than in the tricarbonyl. Unfortunately, the errors in measurement in the former complex, due to the presence of the nine methyl protons, made a detailed analysis of the deuterium distribution impossible, thus precluding a more accurate comparison of the rate of reaction with that of the tricarbonyl.

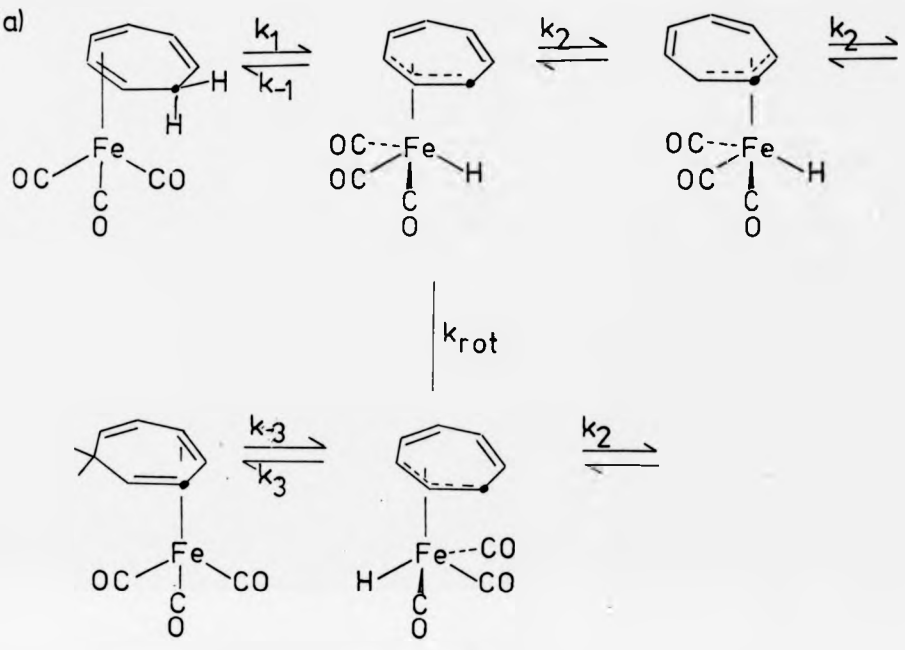
The course of deuteration could, however, be followed in $(C_7H_7D)Fe(CO)_3$, despite errors due to fluctuations in the spectrometer. Fig. [32] indicates the change in the degree of deuteration, at each peak, with time. The four plots A, B, C and D represent the protons of the complexed cycloheptatriene as follows: A = H_2; B = H_1, H_4 and H_5; C = H_3 and H_6; D = CH_2. Repetition of the experiment, (Fig. [33]) indicated that consistent results could be obtained and from the slopes of the lines in both graphs it appears that, within the limits of experimental error, a non-specific scrambling process is occurring. That is, each exchange event is accompanied by equivalencing of all atoms in the cycloheptatriene ring.

t MIN [33]

t MIN [32]

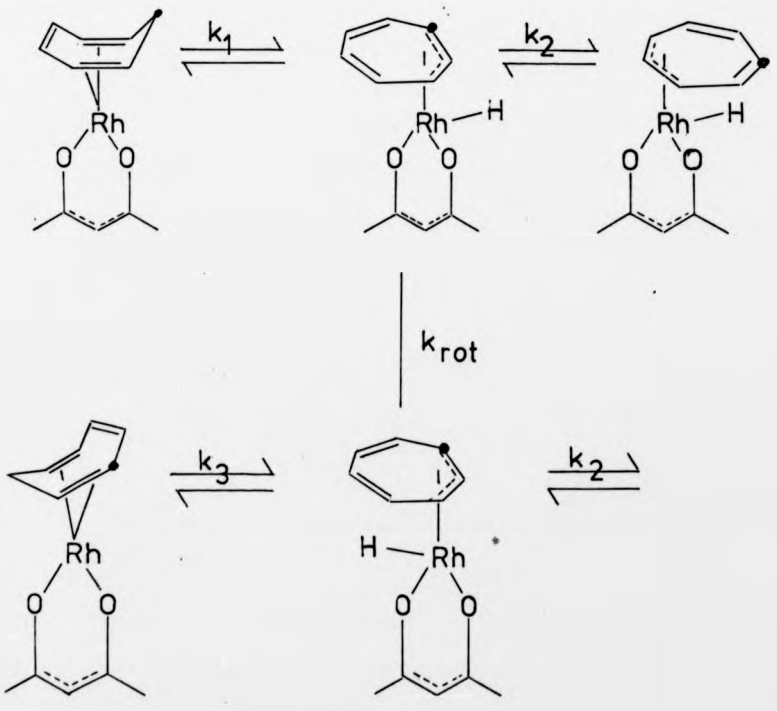
SCHEME 5

(a)



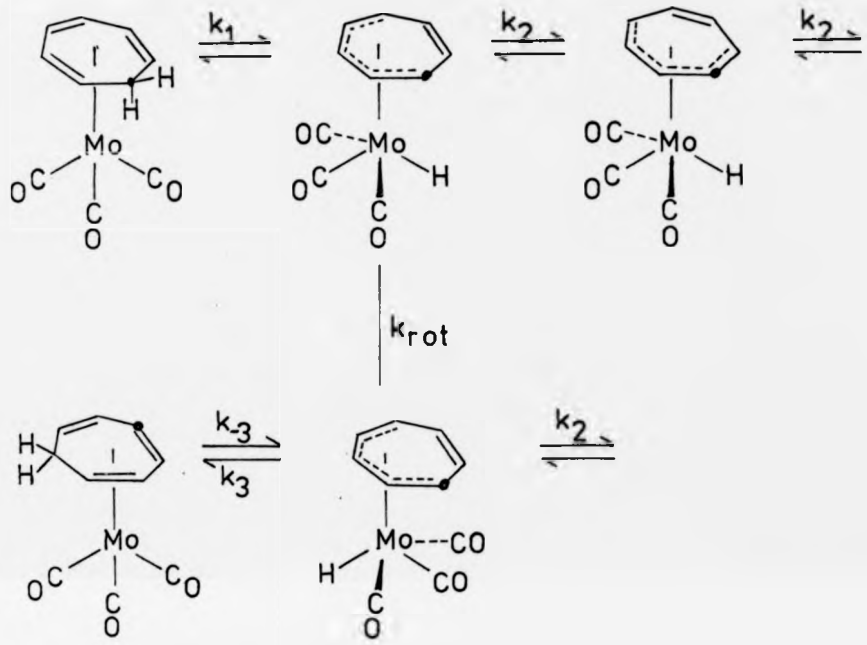
Randomisation if $k_2 \gg k_3, k_{rot}$.

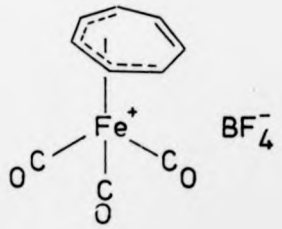
(b)



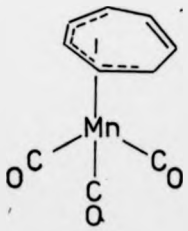
SCHEME 5

(c)





[35]



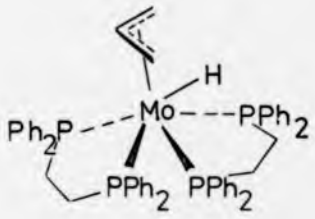
[36]

k_2

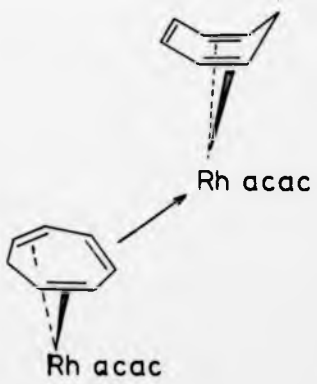
Discussion

The base-catalysed deuteration of both cycloheptatriene and its complexes with iron, have provided further evidence[17,21] for the presence of cycloheptatrienide anion as intermediate in the exchange reaction. Clearly, in the case of the free hydrocarbon, the anion is unstable in solution and readily polymerises, whilst in the complex it is stabilised by the positive charge on the metal. This is confirmed by substituting a superior σ-donor ligand, ($P(OCH_3)_3$ or PPh_3) in place of a carbonyl group in $C_7H_8Fe(CO)_3$ which causes a marked decrease in the rate of the exchange reaction due to a lowering of positive charge on the metal, inhibiting formation of the anionic intermediate.

The successful preparation of cycloheptatriene rhodium (I) acetylacetonate, together with its characterisation as an h^2,h^2 bonded complex, provided an opportunity to compare hydrogen migrations in its cycloheptatriene ring with those in the h^4 iron complex. These experiments demonstrate that two complexes of different but well defined geometry both undergo migration of hydrogen with randomisation (within experimental error) of ring atoms. This is in contrast to earlier work of Pauson and others,[16] where specific 1,5 endo-migration in substituted chromium and molybdenum complexes could be demonstrated. The explanation must lie in the relative labilities of different metal hydride intermediates towards valence tautomerism involving the cycloheptatriene ring. It was suggested by Pauson and Knox[16] that a discrete metal-hydride is not involved although in the absence of definitive evidence it is simpler and more economical to invoke hydrides in all cases. According to Scheme 5, the distinction between specific and random hydrogen shifts lies in the relative rates of return (k_3) and degenerate isomerisation (k_2). The former reaction is known to be fast in the case of the h^5-iron[23] and maganese[24] complexes, [35] and [36], which show dynamic interchange on an N.M.R. time scale. No comparable stuies on h^3-tropylium complexes exist unfortunately.



[37]



[38]

It can, however, be inferred that h^3-allyl metal hydride complexes may rapidly interconvert with the corresponding olefin complex, as is observed in the case[25] of [37] where rapid interconversion between the metal hydride and terminal ligand hydrogens is observed by N.M.R.

If Pauson's results are also applicable to the unsubstituted system, then it suggests a dichotomy between h^3 and h^5 allyl hydride intermediates. The former degenerate rapidly whilst the latter maintain integrity for sufficient time to undergo specific shifts. Possibly the mechanism involves transient formation of a σ-allyl in the former case, although in the absence of definite evidence, a variety of alternative mechanisms might be proposed. The fact that two allyl complexes of very different structure behave similarly in giving random scrambling suggest that this may be a general phenomenon.

The iron complex [14] undergoes endo-specific hydrogen migrations. (Exo-migration could not be observed, since no structural changes are induced), but this can only be inferred in the case of the rhodium complex [11]. Here it appears that ligand exchange is competitive with hydrogen migration since an endo-specific process is apparent in the early stages, only to become increasingly random as isomerisation approaches completion. Since cycloheptatriene has a free double bond in its rhodium complexes, and associative reactions of square planar rhodium species occur readily, a mechanism for intermolecular olefin exchange via [38] may be readily envisaged. Alternatively, traces of free cycloheptatriene produced by decomposition may promote the exchange. In the iron complex, which is co-ordinatively saturated, no such exchange would be expected to occur.

The conclusion of random hydrogen migration would be placed on a much firmer basis if a more fully deuterated cycloheptatriene could be successfully synthesised. The present work demonstrates that although direct synthesis of [$^2H_7$]-cycloheptatriene specifically protonated in the

7 position is possible, it is not very practicable by current synthetic routes. A synthesis of 7- [^{13}C] labelled cycloheptatriene would be very beneficial to this and related studies.

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CHAPTER 3

EXPERIMENTAL

3:1 Cycloheptatriene rhodium acetylacetonate

Bis-(ethylene) rhodium acetylacetonate, (2.0g), was dissolved in diethyl ether, (25ml) and cooled to $0^{o}C$. Redistilled cycloheptatriene, (1.0g) in diethyl ether (10ml) was added to the rhodium complex with stirring. The mixture was stirred overnight and allowed to come to room temperature. It was filtered, about two-thirds of the ether removed and the remainder cooled to $-78^{o}C$ producing orange crystals of cycloheptatriene rhodium acetylacetonate. The rest of the ether was removed and the product recrystallised twice from iso-pentane and dried under vacuum. (1.95g, 85%) (Found : C, 49.01: H, 5.51; O, 10.67: Rh, 34.48 (Rh, 35.69%)*. $C_{12}H_{15}O_2Rh$ required C, 48.98: H, 5.10: O, 10.88: (Rh, 35.03%). ^{1}H. N.M.R. in C_6D_6 gave τ4.86(Acac C-H) 8.25(AcacCH$_3$) 3.97(H_3, $J_{2,3}$ <2Hz) 6.82(H_2) 5.91(H_1, $J_{1,2}$ 10Hz, $J_{1,7\text{-exo}}$ 4Hz, $J_{1,7\text{-endo}}$ 7.5Hz) 6.44($H_{7\text{-endo}}$, J(Rh)$_{7\text{-endo}}$<1Hz) 7.26($H_{7\text{-exo}}$, J(Rh)$_{7\text{-exo}}$ 4Hz, $J_{7\text{-exo},7\text{-endo}}$ 13Hz) ppm.

3:2 Triphenylmethyl tetrafluorcborate

Triphenyl methanol, (4.5g) in propionic anhydride, (45ml) was cooled to $15^{o}C$ and fluoroboric acid (5ml) was added slowly, keeping the temperature below $15^{o}C$. After 30 minutes at $0^{o}C$ the mother liquor was removed, the orange precipitate washed five times with cold ether and dried under vacuum, (5.5g, 97%).

3:3 Tropylium tetrafluoroborate

(i) Triphenylmethyl tetrafluoroborate (2.40g) was dissolved in the minimum volume of acetone (50ml) and excess cycloheptatriene (1ml) was added. The reaction mixture turned from orange to pale yellow in 45 seconds. On addition of diethyl ether, (100ml) white tropylium tetrafluoroborate precipitated out, (0.52g, 40%).

* Subsequent Analysis

(ii) Triphenylmethyl tetrafluoroborate (2.34g) was dissolved in the minimum amount of acetic anhydride (45ml) and excess cycloheptatriene, (1ml) added. Colour changed from orange to yellow in 45 seconds. Addition of diethyl ether (90ml) resulted in precipitation of tropylium tetrafluoroborate, (1.21g, 96%).

3:4 Reaction of Cycloheptatriene rhodium acetylacetonate with diazomethane

Diazomethane was prepared by a standard method from p-toluene sulphonyl-methylnitrosamide. Excess diazomethane (0.1g) in ether solution (5ml) was added to an ether solution of (C_7H_8)Rhacac, (0.5g in 10ml), resulting in a colour change from yellow to brown and precipitation of rhodium No evolution of nitrogen was observed. Excess diazomethane was destroyed with a few drops of acetic acid, the product filtered and ether and acetic acid removed by vacuum distillation. ^{1}H N.M.R. spectra indicated that the products were complex.

3:5 Reaction of cycloheptatriene rhodium acetylacetonate with triphenylmethyl tetrafluoroborate

Triphenylmethyl tetrafluoroborate (220mg) in methylene chloride (20ml) was added to cycloheptatriene rhodium acetylacetonate (200mg) in diethyl ether (20ml). After two hours, fractional crystallisation from pentane gave starting material in high yield (180mg, 90%).

3:6 Degredation of cycloheptatriene rhodium acetylacetonate in deuterochloroform

Cycloheptatriene rhodium acetylacetonate (100mg) was allowed to stand for eight hours in deuterochloroform at 60^{o}C. The initially orange solution turned dark brown and precipitation occurred. 10% aqueous sodium cyanide (5ml) was added, the organic layer removed and dried over anhydrous magnesium sulphate. Filtration and crystallisation produced

acetylacetonylcycloheptatriene, [16] in low yield (10mg, 15%) m.p. and mixed m.p. 124°C.

3:7 Synthesis of 7-[$^2H_1$]-cycloheptatriene

Tropylium tetrafluoroborate (1g) was dissolved in triethyleneglycol dimethyl ether (triglyme),(15ml). Excess lithium aluminium deuteride (0.7g) was added, with stirring. After stirring for 10 minutes, C_7H_7D was removed by trap-to-trap vacuum distillation. (200mg, 38%) 95% C_7H_7D by ^1H N.M.R. in $CDCl_3$. (Triplet centred at 7.74τ, CH_2, integral 2 protons, collapses to a broad resonance, integral 1.05 protons, CHD: quartet centred at 4.62τ, H_1, collapses to a triplet due to loss of couplingwith one proton of CH_2 group, $J_{1,7}$ 7Hz).

3:8 Deuterium scrambling in 7-[$^2H_1$]-cycloheptatriene rhodium acetylacetonate

Samples were dissolved in C_6D_6 in N.M.R. tubes, and placed in water baths at the appropriate temperatures (60 and 75°C). The spectra were run at the ambient temperature of the spectrometer. For the experiment at 60°C spectra were taken at t = 0; 30; 90 and 1080 minutes on a 60MHz Perkin Elmer R.12 spectrometer, and the relative intensities of resonances estimated by duplicate tracings and weighings, (Table 1). At 75°C the spectra were taken at t = 0; 10; 30; 52 and 78 minutes on a 90 MHz Bruker spectrometer, relative intensities being determined from machine print-out, (Table 2).

3:9 Base catalysed deuteration of cycloheptatriene

(i) Cycloheptatriene (500μl) was added to 2.0ml of a 0.96M solution of potassium t-butoxide in d_6 DMSO and heated at 75°C for 90 seconds, after which time, lack of change in the N.MR. spectrum indicated that exchange equilibrium had been reached. The solution was then quenched with D_2O and

centrifuged. The upper (cycloheptatriene) layer was removed and reacted again with an excess (4:1 by volume) of the $KOBu^t/d_6DMSO$, quenched and separated. This process was repeated three more times after which the cycloheptatriene was distilled trap-to-trap under vacuum, (15μl, 3%). Comparison with a standard solution of cycloheptatriene in C_6D_6 indicated that the product was 95% C_7D_8.

(ii) Cycloheptatriene (600μl) was added to 0.96M $KOBu^t$/proteo-DMSO, heated at 75°C for 90 seconds, quenched with H_2O, the organic layer removed and the cycloheptatriene removed by distillation, (360μl, 60%), polymeric residue.

The experiment was repeated with a second 600μl aliquot, the sequence of operations being carried out twice before the cycloheptatriene was distilled off, (110μl, 18%).

(iii) Cycloheptatriene (600μl) was added to 0.96M $KOBu^t$/proteo-DMSO and heated at 75°C for 90 seconds. The cycloheptatriene was distilled off without quenching the reaction mixture with water. Three hours long path trap-to-trap distillation yielded 300μl of cycloheptatriene (50%).

(iv) A molar solution of $KOBu^t$ in H.M.P.A. (8ml) was allowed to come to temperature in a water bath at 75°C. A solution of cycloheptatriene (500μl) in d_6 D.M.S.O. (2ml) was syringed in and allowed to react for 40 seconds at 75°C. The colour which was originally cherry red, changed during the course of the reaction to deep blue. The reaction was quenched by adding D_2O followed by a small amount of isopentane to extract the cycloheptatriene. The isopentane was removed by warming to 40°C leaving deuterated cycloheptatriene (400μl, 80% yield - 60% deuteration by N.M.R.). The process was repeated four more times until a 95% deuteration was achieved. (Final yield of deuterated cyclo heptatriene, 100μl, 19%).

3:10 Cycloheptatriene iron tricarbonyl

To $Fe_3(CO)_{12}$ (31g) was added cycloheptatriene, (9.7ml, 8.5g) in heptane (86ml). The mixture was refluxed for three hours and then distilled between -5 10°C at 1mm Hg, to remove solvent and iron pentacarbonyl ($Fe(CO)_5$). The residue was dissolved in pentane, filtered and distilled under high vacuum. The fraction distilling at 46°C and 10^{-2} mm Hg being collected, and chromatographed on a basic alumina column using 40-60 petrol. The first fraction eluted was h^4-(1-4) cyclohepta-1,3-diene iron tricarbonyl (m.p.24°C. N.M.R. resonances at 4.75, 7.00, 8.05 and 8.60τ[1]). This was followed by cycloheptatriene iron tricarbonyl [14], (8.9g, 40% m.p.6°C, N.M.R. in CCl_4 gave τ 4.25(H_2, $J_{1,2}$ 10.6Hz, $J_{2,3}$ 7.7Hz); 4.85 (H_1): 4.76(H_4, H_5, $J_{4,5}$ 4.74Hz, $J_{3,4}$ 7.7Hz); 6.70(H_3): 7.04(H_6) and 7.7(CH_2)p.p.m.)[1].

3:11 Double resonance studies

The spectra, recorded on a Perkin-Elmer R.12 spectrometer, were of approximately 2M benzene solutions of cycloheptatriene iron tricarbonyl and cycloheptatriene iron dicarbonyltrimethylphosphite, (300μl in 5mm N.M.R. tubes). Double irradiation was performed at each of the resonance positions for protons H_1-H_6 and the intensity of the corresponding protons (H_6-H_1) was monitored by recording the integral of the resonance. No change in intensity was observed at any position for either compound, although the expected decouplings occurred.

3:12 Reaction of cycloheptatriene iron tricarbonyl with base

(a) $C_7H_8Fe(CO)_3$, (135mg) was added to 300μl of a molar solution of potassium t-butoxide in hexamethylphosphoramide in a 5mm N.M.R. tube. The solution immediately turned a deep red colour and an N.M.R. spectrum of this solution indicated that the starting material had all been converted to

the anion $C_7H_7Fe(CO)_3^-$, (sharp singlet 5.35τ). On addition of CD_3OD (400μl) the peak at 5.35τ disappeared. The complex was extracted with isopentane, and an N.M.R. spectrum taken in d_6 benzene indicated that the intensity of the resonance centred at 8.00τ, ($-CH_2$ of $C_7H_8Fe(CO)_3$) had been reduced to about half its original value, [23]. The extract in benzene was then heated at 100°C for one hour and a second N.M.R. spectrum taken [24].

(b) $C_7H_8Fe(CO)_3$, (200mg) was added to (i) a 0.8M solution of $[^2H_3]$-sodium methoxide in $[^2H_4]$-methanol (500μl) and (ii) a 0.435M solution $[^2H_3]$-potassium methoxide in $[^2H_4]$-methanol (500μl) in separate N.M.R. tubes. After one hour at 33°C the cycloheptatriene complex was extracted with isopentane and N.M.R. spectra taken in d benzene. In both cases the spectra of the products were identical to [23] above, giving exo-$[7-^2H_1]$ cycloheptatriene iron tricarbonyl, 90% $[^2H_1]$.

Repeating the experiment at 120°C for 30 minutes in a sealed N.M.R. tube, resulted in the decompositon of the complex.

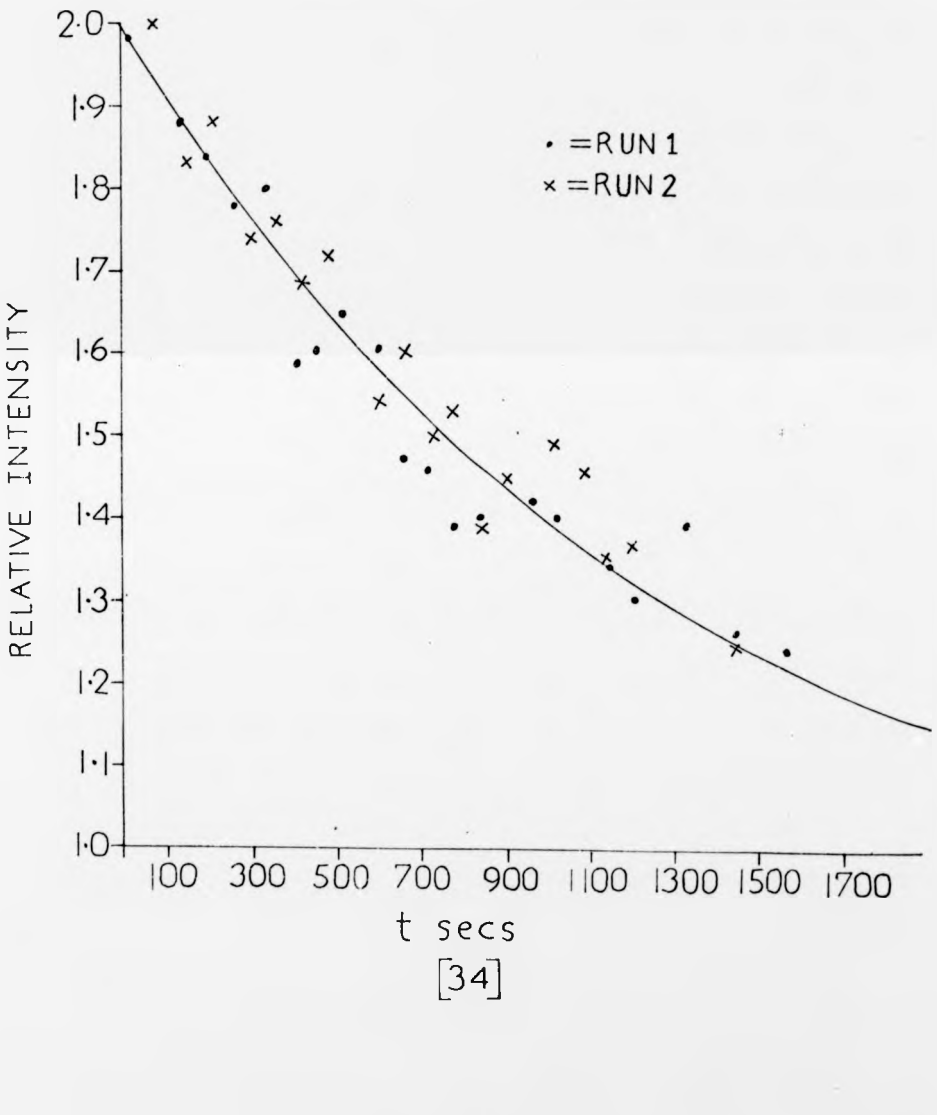
3:13 Ultra-violet irradiation of $[^2H_1]$ cycloheptatriene iron tricarbonyl

$C_7H_7DFe(CO)_3$ (140mg) was dissolved in d_6 benzene (400μl) in a small silica tube and irradiated for 5 hours with a Hanovia 509/12, 500W, medium pressure, mercury arc lamp.

Inspection of the solution indicated that decomposition had occurred and an N.M.R. spectrum revealed the presence of free cycloheptatriene.

3:14 Preparation of cycloheptatriene iron dicarbonyl trimethylphosphite

A mixture of $C_7H_8Fe(CO)_3$, (5ml, 6.7g) and trimethylphosphite (35ml) was stirred and heated at 60°C for 4 days. Excess $P(OCH_3)_3$ was then removed at 20°C/10 mm and the residue distilled onto a cold finger trap at 70°C/10^{-3}mm. The distillate contained some $Fe(CO)_2(P(OCH_3)_3)_3$, (10% by N.M.R.) Chromatography of this material in 40% diethyl ether in light petroleum


2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
RELATIVE INTENSITY
• =RUN 1
× =RUN 2
100 300 500 700 900 1100 1300 1500 1700
t secs

[34]

on a neutral alumina column yielded a yellow, air-stable liquid which on crystallisation at -78°C from isopentane gave cycloheptatriene iron dicarbonyl trimethylphosphite, (4.5g, 48%: N.M.R. in d_6 benzene gave τ4.15(H_2); 4.88(H_1); 5.14(H_4,H_5); 6.72(-OCH_3); 7.10 broad multiplet (H_3,H_6) and 7.70(CH_2)p.p.m.)

3:15 Kinetic studies of base-catalysed deuterium exchange in $C_7H_8Fe(CO)_3$ and $C_7H_8Fe(CO)_2P(OCH_3)_3$

(i) To $[^2H_3]$-potassium methoxide in $[^2H_4]$-methanol (0.435M, 350μl) in an N.M.R. tube, was added $C_7H_8Fe(CO)_3$ (100μl) at 33°C, the temperature of the N.M.R. probe. The tube was stoppered, shaken and an N.M.R. spectrum immediately taken. Subsequent spectra, taken at regular intervals, monitored the peaks at 4.25τ(H_2) and 7.7τ(CH_2), until there was no further change.

(ii) A solution of $C_7H_8Fe(CO)_2P(OCH_3)_3$ was made up in an identical manner to the above and N.M.R. spectra taken, monitoring the peaks at 4.23τ(H) and 4.78τ(CH_2).

In both exchange reactions the intensities of the peaks were determined by cutting out and weighing photocopies of the resonances. The relative change in intensity, due to deuteration, of the -CH resonance was given by $I(CH_2)/I(H_2)$ where I is the absolute intensity of the resonance. A t = 0 spectrum was given by 100μl of the complex in $[^2H_4]$-methanol (350μl). Extrapolation of a plot of relative intensity against time, [34] gave a t_∞ of 1.12 protons at the CH_2 position.

3:16 Kinetic study of deuterium scrambling in $C_7H_7DFe(CO)_3$ and $C_7H_7DFe(CO)_2P(OCH_3)_3$ at elevated temperature

(i) $C_7H_7DFe(CO)_3$ (100μl) was dissolved in d_6 benzene (350μl) in an N.M.R. tube, and an N.M.R. spectrum taken. The tube was then placed in a water bath at 75°C for 5 minutes, after which a second spectrum was taken. This process was continued until there was no further change in the N.M.R. spectrum.

As in the exchange reaction, the intensities of the resonances were determined by duplicating and weighing. Values were obtained for the four distinct resonances, A(H_2); B(H_1,H_4 and H_5); C(H_3 and H_6) and D(CH_2), of cycloheptatriene iron tricarbonyl. Relative intensities were determined by dividing the weight of one resonance by the total weight of all resonances at time t. A plot was then obtained of relative intensity against time for each resonance A-D (see Figs. [32] and [33])

(ii) $C_7H_7DFe(CO)_2P(OCH_3)_3$ (100μl) was dissolved in d_6 benzene (350μl) in an N.M.R. tube and the reaction monitored as in (i) above. In this case the four distinct resonances were - A(H_2); B(H_1, H_4 and H_5); C(H_3,H_6 and 3 x CH_3) and D(CH_2). The presence of the methyl groups caused large errors in the relative intensities, thus precluding reasonable graphical comparison.

3:17 Preparation of cycloheptatriene iron dicarbonyl triphenylphosphine

$C_7H_8Fe(CO)_3$, (880mg) was dissolved in acetone (300ml), triphenylphosphine (990mg) added, and the solution irradiated in a 250 watt photolyser for 20 hours. An I.R. spectrum of the solution revealed the presence of starting material, (carbonyl absorptions at 2050, 1989 and 1975 cm^{-1}), bis(triphenylphosphine)iron tricarbonyl (C = O at 1894cm^{-1}) and $C_7H_8Fe(CO)_2PPh_3$(C = O at 1973 and 1920cm^{-1}). Chromatography, in dichloromethane on neutral alumina, produced a yellow oil which on recrystallisation from light petroleum yielded $C_7H_8Fe(CO)_2PPh_3$, identified by its infra-red spectrum, (760mg, 43%)